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Project Director: Dr. W. R. Ernst

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GEORGIA INSTITUTE OF TECHNOLOGY
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Date: 5/4/81

Project Title: An Experimental Study of the Performance of Non-Uniformly Active Catalysts.

Project No: E-19-669

Project Director: Dr. W. R. Ernst

Sponsor: National Science Foundation

Effective Termination Date: 1/31/81

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- ☒ Final Fiscal Report (FCTR)
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A Progress Report for the National Science Foundation

Project No. ENG-78-00731 for the

Period 8/15/78 - 8/15/79

An Experimental Study of
Nonuniformly Active Catalysts

by

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September 15, 1979

Progress Report for ENG 78-00731 for the Period 8/15/78 to 8/15/79

Introduction

During the first year of the program we focused our efforts on (1) developing reproducible methods of preparing catalysts with various radial profiles of Pt; (2) on developing methods of characterizing the Pt profiles by electron probe microanalysis; (3) on applying other methods of characterizing the catalysts, such as X-ray fluorescence, X-ray line broadening and hydrogen chemisorption; (4) on procuring, erecting and testing equipment for catalyst preparation, characterization, and reaction experiments; and (5) on conducting a few deuterium-hydride exchange reaction experiments. This report is written in two parts. Part I describes major equipment items as well as results of several reaction experiments. Part II is a copy of a manuscript recently accepted for publication by Journal of Catalysis. It describes experiments we conducted which led to a new catalyst preparation technique and describes our efforts in characterizing the catalysts by electron probe microanalysis.

PART I

I. Experimental Equipment

A. Vacuum system

All of the major equipment required for catalyst preparation, characterization and reaction experiments has been procured, erected and tested. Most of the equipment has been incorporated into a general purpose vacuum system. This system consists of a vacuum (Pyrex) manifold with connections to storage bulbs for deuterium, neopentane, hydrogen, and helium; to pressure and vacuum gauges, to vacuum pumps, to the reaction system and to a hydrogen chemisorption apparatus. High vacuum (10^{-7} torr) is provided by a new Edwards Cryo-cooled pumping system. All equipment was purchased within the last twelve months. Table A1 provides details of this equipment.

B. Reaction system

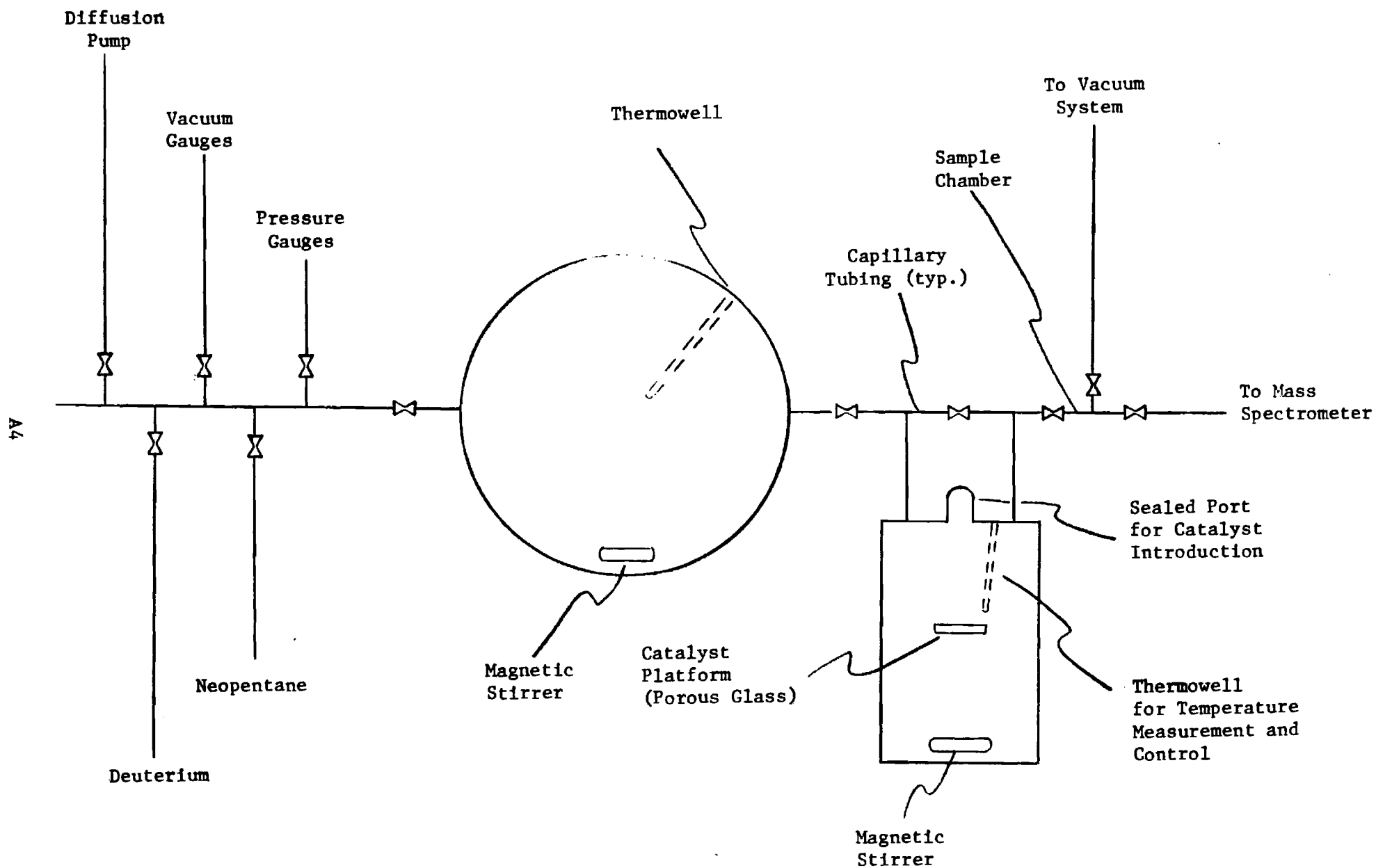
The reaction system shown schematically in Fig. A1 consists of a 1000 cm^3 spherical Pyrex vessel for premixing deuterium and neopentane and a 500 cm^3 cylindrical Pyrex reaction vessel wrapped with Nichrome wire and insulation and containing a glass encased magnetic stirrer. A porous glass platform designed to support a spherical catalyst particle extends into the center of the reactor. The reactor has two openings -- one for rapidly introducing premixed reaction gases and one for removing samples. The sample connection consists of two stopcocks which isolate a 2.5 cm^3 volume. The discharge end of the sample connection is attached directly to the ionization chamber of a new Kratos MS-10S mass spectrometer. A thermowell which extends to the center of the reactor just above the catalyst platform, contains an Iron - Constantan thermocouple. Temperature control is accomplished with a Leeds and Northrup Electromax III controller in conjunction with a Leeds and Northrup Zero Voltage Power Pack which applies current to the

Table A1

Components of Experimental Apparatus for Deuterium-hydride Exchange Experiments, Hydrogen Chemisorption, and Catalyst Drying and Reduction.

<u>Equipment</u>	<u>Function</u>	<u>Purchased by</u>
Kratos MS10S mass spectrometer with 10-300 mass range modified to allow continuous variation of electron beam energy between 10 and 70 eV.	Analysis of D-exchanged isomers of neopentane	Georgia Tech (cost sharing)
Edwards CR63 Cryo cooled high vacuum pumping system with Pirani and Penning gauges	Provides vacuum for glass manifold system which includes H ₂ chemisorption apparatus and D-exchange reaction system.	Georgia Tech (cost sharing)
MKS Baratron Type 220 manometer, range 0.1 to 1000 torr	Pressure gauge for H ₂ chemisorption apparatus	Georgia Tech (cost sharing)
MKS Baratron Type 220 manometer, range 0.1 to 100 torr	Pressure gauge for D-exchange reaction experiments	NSF
MKS PDR-2	Pressure read out unit for both MKS Baratron manometers	Georgia Tech (cost sharing)
Leeds and Northrup Electromax III Controller and Zero Voltage Power Pack	Reactor Temperature Control	NSF
Tecam Fluidized bed (Sand bath)	Controlled heating of catalyst sample during drying calcination and reduction.	NSF
Thermolyne Tube Furnace	Bake out of sample for H ₂ chemisorption experiments	NSF

Figure A1. Equipment for Deuterium-Neopentane Exchange Experiments (Some details not shown)



Nichrome wire surrounding the reactor.

C. Hydrogen chemisorption system

The hydrogen chemisorption system is constructed of Pyrex except for a quartz sample holder. The system is designed for static volumetric chemisorption experiments at room temperature. Pressure is measured with an MKS Baratron gauge with a range of 0.1 to 1000 torr. For bakeout of the sample holder, a Thermolyne Tube furnace is used.

D. Catalyst preparation

A Tecam Fluidized Bed provides controlled heating as various gases flow through a catalyst sample container during drying, calcination and hydrogen reduction.

E. Diffusion cell

A diffusion cell, similar to that of Gorring and deRossett (1964), has been constructed from 316 stainless steel. Gaskets for the cell were prepared from a special glass reinforced teflon (RT/Duriod 5801 -- Rogers Corporation of Atlanta, Georgia). This material exhibits almost no gas release when heated to 300°C. It will be possible to determine diffusion coefficients over a wide range of temperatures, from room temperature to the temperature range of the deuterium-hydride exchange reaction experiments.

II. Kinetic Experiments

A. Procedure

Deuterium-neopentane exchange experiments on a single catalyst particle were carried out in the batch reactor system. A catalyst particle was introduced

Gorring, R. L. and A. J. deRossett, "Gas Diffusion in Porous Catalysts. Diffusion-Controlled Elution of Physically Adsorbed Hydrocarbons", J. Catalysis, 3, 341 (1964).

through a 15 mm opening at the top of the reactor. After the particle was positioned on the porous glass platform, the opening was heated with a torch and sealed. (When a new catalyst particle is to be tested, the seal will be broken, the old particle removed, the new particle inserted, and the reactor re-sealed.)

Prior to each experiment the catalyst within the reactor was subjected to high vacuum (5×10^{-7} torr) at reaction temperature for one hour. After the evacuation, all stopcocks on the reactor were closed. The feed gas mixture, consisting of deuterium to neopentane mole ratio of 1000 to 1 was prepared by first charging Matheson C.P. grade neopentane (99.87%) to the premix flask to a pressure of 0.56 mm Hg as determined by a Baratron pressure gauge, and then charging Matheson research grade deuterium (99.5%) to a final pressure of 582.0 mm Hg. The deuterium was further purified by passing it through a "Deoxo" unit and liquid nitrogen trap. After the gases were thoroughly mixed by a magnetic stirrer, they were rapidly transferred to the preheated reactor by opening a stopcock between reactor and premix flask.

Samples were removed batchwise at regular time intervals and analyzed on the mass spectrometer. Sampling consisted of evacuating the sample loop to 10^{-6} torr; then opening the stopcock between the reactor and sample loop to allow the loop to be filled with reaction gases. The stopcock was then closed and the sample loop evacuated to 10^{-6} torr. The stopcock was opened again to allow the loop to be filled with reaction gases. The stopcock was then closed and the stopcock between the sample loop and the mass spectrometer opened. An adjustable leak on the mass spectrometer was used to maintain a steady flow to the ionization chamber. Scans of the mass range, 57 through 66 (C_4H_9 through C_4D_9) were recorded for each sample. Background scans were taken prior to the introduction of each sample in order to correct sample scans for any residual materials present in

the mass spectrometer.

Sample analyses were performed at a low electron beam energy of 15 eV in order to minimize fragmentation of the $C_4D_1H_{9-1}$ ions. The availability of the mass spectrometer and the ability to interface the reactor has made a substantial improvement in ease of experimentation and analytical accuracy over the previous work (Ernst and Wei, 1975). In that work a mass spectrometer was available only on a time sharing basis. Thus it was necessary to handle and store small volume batch samples of reaction gases. Handling losses undoubtedly affected results. These problems have been eliminated in the current study.

B. Results and Discussion

Four trial reaction experiments on a single uniformly active catalyst bead have been carried out. These experiments covered a range of reaction temperatures from 202°C to 261°C. The catalyst particle had a Pt content of 0.99 wt% and average Pt crystallite size of $<10 \text{ \AA}$ by H_2 chemisorption.

Table A2 presents the raw data (relative peak heights versus time) for each temperature. These data have not been corrected for fragmentation and natural abundances of C_{13} and deuterium. Computer programs are currently being prepared to make these corrections. The data in Table A2 show that all experiments were continued to at least 80 percent conversion of neopentane. The data show that as reaction temperature increased, selectivity toward the more highly D-exchanged isomers increased. (An increase in temperature corresponds to an increase in reaction rate constant hence an increase in Thiele

Ernst, W. R. and J. Wei, "Deuterium-Hydride Exchange in a Single Catalyst Particle", J. Catalysis, 39, 303 (1975).

Table A2

Analyses of Gases during Deuterium-Neopentane
Exchange Reaction Experiments

Run No. H 12		T = 202.1°C						$x_{D_2} = 0.999$		
Time,min	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9
30	51.26	18.95	9.59	6.88	4.08	2.94	2.66	1.88	1.10	0.64
45	43.28	21.29	11.70	5.43	6.22	5.01	2.67	2.67	0.98	0.75
60	34.69	20.38	12.92	9.08	7.64	6.11	4.12	2.96	1.44	0.65
80	25.18	20.21	14.48	11.51	9.52	7.68	5.73	3.43	1.74	0.51
120	14.84	16.87	14.81	13.58	11.48	10.19	7.79	6.22	2.67	1.48
150	9.83	13.92	13.23	13.04	12.92	12.46	10.49	7.71	4.47	1.93
260	1.24	6.69	7.99	9.72	12.06	14.13	15.16	13.92	13.16	5.93
350	1.16	3.79	4.85	7.43	10.27	13.86	16.38	17.02	15.44	9.80

Run No. H 13		T = 218.3°C						$x_{D_2} = 0.999$		
Time,min	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9
12	61.52	14.05	5.76	3.86	2.97	4.18	2.59	2.53	1.90	0.63
21	49.02	16.19	6.62	7.12	4.66	4.16	3.47	3.91	2.27	2.58
35	33.40	16.50	8.51	7.60	6.04	5.98	6.11	5.78	4.81	5.26
50	22.14	15.73	10.31	9.65	6.94	7.40	6.48	7.14	6.08	7.53
72	11.48	10.19	10.43	9.63	8.67	8.35	8.03	10.19	10.19	12.84
100	4.42	8.37	8.29	9.40	8.61	9.16	9.79	12.72	11.85	17.38
190	0	2.01	2.47	3.75	3.75	5.58	7.50	12.08	16.74	46.11

Run No. H 14		T = 241.°C						$x_{D_2} = 0.999$		
Time,min	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9
7	40.44	13.52	6.91	5.71	5.11	4.51	3.91	4.99	4.39	10.52
14	30.61	12.00	7.84	7.02	5.45	6.20	4.77	6.27	4.64	15.20
29	17.39	10.45	7.02	7.09	5.26	6.87	6.10	7.74	7.65	24.41
45	8.53	8.17	6.00	6.00	5.35	7.38	6.22	9.69	9.18	33.48
76	1.35	4.30	3.46	3.96	3.37	5.14	5.56	10.37	11.21	51.26

Run No. H 15		T = 261.1°C						$x_{D_2} = 0.999$		
Time,min	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	d_9
8	58.67	9.56	3.35	4.48	2.59	2.70	3.40	3.78	2.81	8.64
16	38.60	9.33	4.86	5.18	4.02	4.34	4.34	6.02	4.40	18.91
25	24.81	8.56	5.06	5.06	4.72	5.73	4.52	7.28	6.07	28.19
35	15.59	7.5	4.19	4.63	4.12	5.96	4.71	8.82	6.69	37.79
53	5.50	4.85	3.24	3.78	3.24	4.85	4.24	8.78	8.17	53.39

parameter). For example the $m/e = 66$ peak increased with temperature for constant sample time. This finding is consistent with theory of diffusion and reaction within uniformly active catalysts which predicts an increase in selectivity to more highly reacted products with increase in Thiele parameter for series reactions.

Part II

Preparation of Nonuniformly Active Catalysts

by

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ABSTRACT

The effect of adding chemical co-ingredients to H_2PtCl_6 impregnating solutions in order to modify Pt profiles in spherical γ - alumina beads was studied. Co-ingredients included the following acids and salts: HCl , HF , HNO_3 , acetic acid, citric acid, tartaric acid, AlCl_3 , NaCl , NaF , NaBr , NaNO_3 , Na_3PO_4 , Na Benzoate, and Na Citrate. Radial Pt profiles were examined by electron probe microanalysis of bead cross sections. Nine distinctly different types of profiles were produced. NaBr was the only co-ingredient which produced a monotonically increasing Pt profile from bead center to surface. A simple model which describes the role of NaBr during the impregnation process was discussed. A method of producing monotonically decreasing Pt profiles from bead center to surface which involves incorporating both NaBr and citric acid in H_2PtCl_6 impregnating solution was studied.

Introduction

Non-uniformity of activity in supported metal catalysts can occur as a result of catalyst preparation methods or catalyst poisoning. Non-uniformly active catalysts may in some processes, exhibit superior activity, selectivity or resistance to poisoning compared to uniformly active catalysts. Many recent papers have discussed theories of diffusion and reaction in non-uniformly active catalysts (1,2,3,4,5,6). Less attention has been focused on fundamental experimental studies which involve preparation, characterization, and evaluation of performance in kinetic studies involving probe reactions. Several challenging questions arise when one attempts such fundamental studies, e.g., What parameters should be adjusted during catalyst preparation in order to produce a desired distribution of active ingredient within a support particle? Quantitative measurement of mass distribution of active ingredient within a particle can easily be determined for metals by electron probe microanalysis; but, how does one quantitatively measure "activity" distribution within a particle? Is it valid to assume constant diffusivity throughout a non-uniformly active catalyst particle, as often assumed in published models? Experimental verification of model predictions is necessary if one is to have confidence in these models as tools for design.

A recent paper presented the theoretical basis for a kinetic study to determine the effect of activity distribution in spherical catalyst particles on selectivity of the deuterium-hydride exchange reaction (7). The catalyst considered was alumina supported platinum. (This reaction was shown previously to be a suitable probe for diffusional influences in uniformly active catalysts (8,9)). This paper presents results of the catalyst preparation phase of this study. A later article will report results of characterization and kinetic studies.

Impregnation was selected as the means of preparing the catalysts because of its simplicity and wide use. Previous workers have developed ways of producing uniform profiles of active ingredient (for example 10,11) and sharply defined profiles such as outer shells, inner shells, and cores (for example 12,13,14). Workers have investigated many preparation variables and their influence on the distribution of active ingredient in a number of metal-support combinations (11,15,16,17,18). There exists a broad body of knowledge of the physical and chemical processes of the impregnation process (for example 19,20,21,22,23,24,25,26,27). However, each metal-support combination is unique and hence introduces new challenges to the investigator.

An objective of this work was to investigate the possibility of using chemical additives (co-ingredients) in impregnating solutions as a means of controlling the distribution of active ingredient within the catalyst particle. Platinum on spherical γ -alumina beads was the system studied. Of particular interest for our future kinetic studies would be the ability to approximately reproduce some of the profiles that are considered in theoretical studies previously mentioned (3,4,5,6) -- for example, profiles which monotonically increase or decrease from particle center to surface. Linearly increasing or decreasing profiles were frequently considered in these theoretical studies.

Catalysts which have monotonically decreasing profiles are of some interest in kinetic studies because they serve as models of partially poisoned catalysts. There may also be commercial interest in such catalysts especially for reactions which are diffusion limited and in which the catalyst undergoes a shell progressive poisoning. They may exhibit activity or poisoning resistance that is superior to uniform or shell profiles.

Hexachloroplatinic acid was the active ingredient selected for this study. The strong interaction between H_2PtCl_6 and γ -alumina is known to produce shell

catalysts which have a well defined boundary between Pt and bare support. Citric acid was employed as an additive to the H_2PtCl_6 solution because this combination is known to produce core catalysts. The approach that was used to find a means of controlling Pt profile was: first to explore the interactions of H_2PtCl_6 and citric acid with the alumina supports; second, to experimentally survey a large number of chemical additives which, when included in the impregnating solutions, modify the shell or core profile; and third, to select and further investigate the chemical additive which yields the Pt profiles desired.

Experimental Methods

A 0.0564 M stock solution of H_2PtCl_6 was prepared by dissolving Fisher Certified $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in deionized and carbon treated water. Solution concentrations were determined by a spectrophotometric method (28) on a Bausch and Lomb spectrophotometer. Concentrations were expressed as moles of Pt per liter. A 0.1 M stock solution of citric acid (CA) was prepared from Fisher Certified CA. Solution concentrations were determined by titration. Stock solutions of various acids or salts (Table 1) were prepared to give concentrations of about 0.1 M. Gamma-alumina beads of spherical geometry (Rhône Poulenc Inc., GOD-30) had the following properties: diameter, 0.36 cm; bulk density, 0.3 g/cm³; surface area, 150 m²/g; total pore volume, 1.70 cm³/g and average pore diameter, 450 Å.

Adsorption isotherm experiments involved contacting eight (8) alumina beads (ca. 0.1 gm) with 0.5 cm³ of solution containing CA or H_2PtCl_6 at 25°C. All solutions were prepared by diluting the stock solutions described above. After two (2) hours of contacting, beads were separated from solution by filtration and washed with 2 cm³ of water to quantitatively remove and recover external solution. Washing time and volume were kept to a minimum to avoid removal of active ingredient from pore solution. The recovered solution was

Table 1. Properties of Co-Impregnated Catalysts

Acid or Salt	Impregnation Time, 1 hour					Impregnation Time, 22 hour		
	Conc(M)	Pt(wt%)	Pt Band, r/R			Conc(M)	Pt(wt%)	Pt Band
			Begins at	Ends at	Type			
None	-	0.51	1	0.77	1	-	0.51	2
AlCl ₃	0.01	0.50	1	0.56	1	0.01	0.51	2
HCl	0.01	0.51	1	0.67	1	0.01	0.50	2
NaCl	0.01	0.49	1	0.81	1	0.01	0.51	2
HF	0.01	0.50	-	-	5	0.01	0.50	5
NaF	0.01	0.51	1	0.83	1	0.01	0.51	2
NaBr	0.01	0.50	1	0.77	1	0.01	0.50	9
HNO ₃	0.01	0.50	1	0.50	1	0.01	0.51	3
NaNO ₃	0.008	0.49	1	0.79	1	0.008	0.51	2
Na ₃ PO ₄ (a)	0.01	0.31	0.83	0	7	0.01	0.10	8
Na Benzoate	0.01	0.48	1	0.78	1	0.01	0.50	2
Acetic Acid	0.01	0.51	-	-	3	0.01	0.50	Uniform
Citric Acid	0.01	0.49	0.84	0.44	4	0.01	0.48	6
Na Citrate (a)	0.02	0.19	0.33	0	7	0.01	0.14	8
Tartaric Acid	0.01	0.49	-	-	6	0.01	0.51	7

Footnotes for Table 1

- (a) The 22 hour sample was prepared using a fresh solution of Na₃PO₄ (or Na Citrate) and H₂PtCl₆ while the 1 hour sample was prepared using a portion of that same solution after it had been stored for 2 or 3 days.

diluted with water to a volume of 5 cm³ and analyzed for active ingredient. The amount of adsorption was determined by the difference between initial and final concentrations of active ingredient in solution after correcting for pore volume.

In experiments designed to test a large number of acids and salts as co-impregnating ingredients, solutions were prepared by adding stock solutions of H₂PtCl₆, acid or salt solution, and water in the volumetric ratio, 1:1:8. The experimental procedure involved placing eight (8) alumina beads in contact with 0.5 cm³ of impregnating solution for 1 hour or 22 hours at 25°C. The beads were removed from solution, washed with 2 cm³ of water, dried in air at 120°C for eight (8) hours and reduced in flowing H₂ at 500°C for one (1) hour. Residual impregnating solution combined with wash water was analyzed for Pt. Characterization as to the type of Pt profile was determined by visual observation or by electron probe microanalysis (EPM) of beads that had been cleaved in half (29). EPM was performed on an Acton MS-64 microprobe using a point count technique. Beads that had been cleaved in half were scanned across the flat side through the bead center. Thirty second counts were taken at 100 μm intervals across the surface. Scans at one to four orientations were taken for each bead. Data smoothing consisted of averaging the scan data taken at all orientations and reporting the averaged and normalized Pt profile from bead center (r/R=0) to surface (r/R=1). Visual observation was used when the profile was obviously a shell or core type with a sharp boundary between Pt and bare support. EPM was used when the profile was diffuse.

More extensive co-impregnation studies using solutions prepared from various combinations of H₂PtCl₆, CA, and NaBr stock solutions and water of dilution were conducted in a manner similar to the above experiments; however,

in the more extensive studies, the effects of impregnation time, NaBr and CA concentrations on final Pt profile were studied. EPM was used in determining Pt profiles for all samples.

Results and Discussion

a. Adsorption Studies

Adsorption plays a large role in the impregnation of γ -alumina with H_2PtCl_6 solution. The bonding between Pt complex (henceforth referred to as Pt) and the surface is not well understood although mechanisms have been suggested (for example 25,27).

Fig. 1 shows the total uptake of Pt after beads were contacted for two (2) hours with impregnating solution containing H_2PtCl_6 , then washed, dried, and reduced. The ordinate of this graph "total Pt uptake" takes into account both adsorbed Pt and Pt deposited from pore solution during drying. The solid line shows the trend of the data. The dotted 45° line is a theoretical line for irreversible adsorption. The fact that data points at initial Pt values of about 0.006 moles and below, fall near the theoretical line shows the strong interaction between Pt and γ -alumina. The other dotted line shows the trend of data at large values of initial Pt. The increase in the total Pt uptake in this linear region is due to Pt deposited from pore solution during drying. The intersection of the two dotted lines represents the Pt uptake at saturation coverage of adsorption sites. The saturation coverage, 0.012 mmols Pt, divided by alumina sample weight and surface area corresponds to 110 μ moles/g and 750 μ moles/m² respectively.

Fig. 2 is a similar graph for the total uptake of CA. As in the case of Pt, data points at low initial CA fall near the dotted 45° line thus showing a strong interaction between CA and γ -alumina; at large initial CA the data trend is linear. Intersection of the two dotted lines, which corresponds

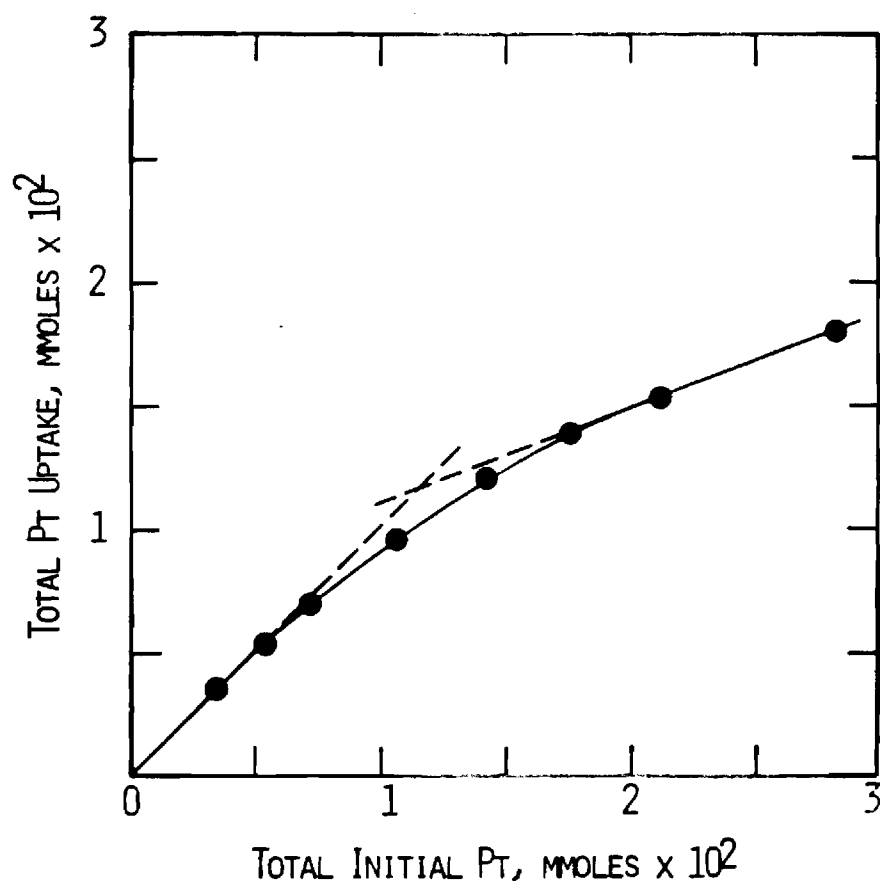


Figure 1. Total uptake of Pt from impregnating solution by γ -alumina.

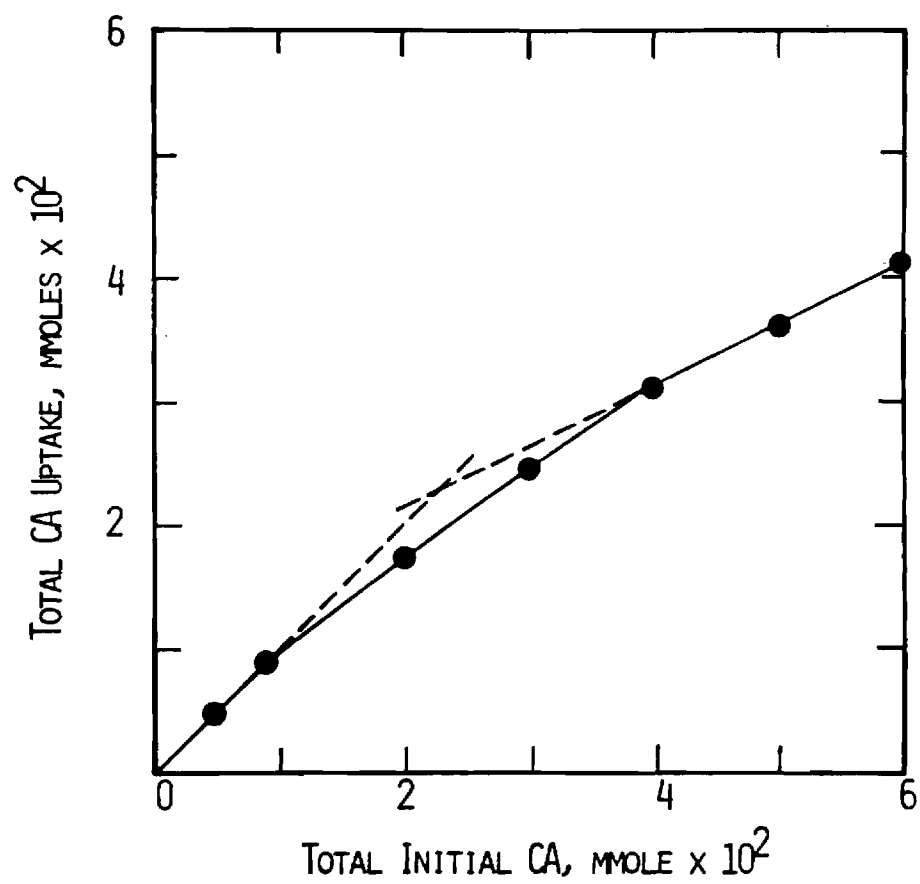


Figure 2. Total uptake of CA from impregnating solution by γ -alumina.

to saturation coverage of adsorption sites, occurs at 0.023 mmoles CA. Saturation coverage divided by sample weight and surface area equals 215 $\mu\text{moles/g}$ and 1433 $\mu\text{moles/m}^2$ respectively or approximately twice the saturation coverage for Pt.

Adsorption isotherms (Fig. 3) were determined for both Pt and CA from data in Figs. 1 and 2 by subtracting the pore volume contribution from total uptake. The isotherms are expressed in terms of percent of adsorbed species. The line through the Pt data corresponds to the Langmuir equation:

$$\text{Wt\% Pt} = \frac{2880C}{1 + 1286C}$$

The CA data do not conform to the Langmuir model. A line was drawn however to show the trend of the data.

b. Effect of Co-ingredients on Pt Profile

Table 1 presents a list of acids and salts which were studied in a set of co-impregnation experiments. The purpose was to screen a large number of chemicals as co-ingredients with H_2PtCl_6 to determine their effects upon the final Pt profile in the alumina beads. It was desirable to examine these effects after relatively short (1 hr) and long (22 hr) impregnation times, and to eliminate profile changes over this time period due to Pt diffusing into the pores from external impregnating solution. To avoid this undesirable effect, the total amount of Pt and total volume of solution were kept low -- total Pt in solution was about 23 percent of the amount required to saturate the adsorption sites in the alumina (Fig. 1); solution volume was about 2.7 times the pore volume. Under these conditions, at short impregnation time, the solution would become essentially depleted of Pt as the Pt adsorbed on the support thus substantially reducing any driving force for diffusion. A control experiment in which no co-ingredient (Table 1, first entry) was added to the

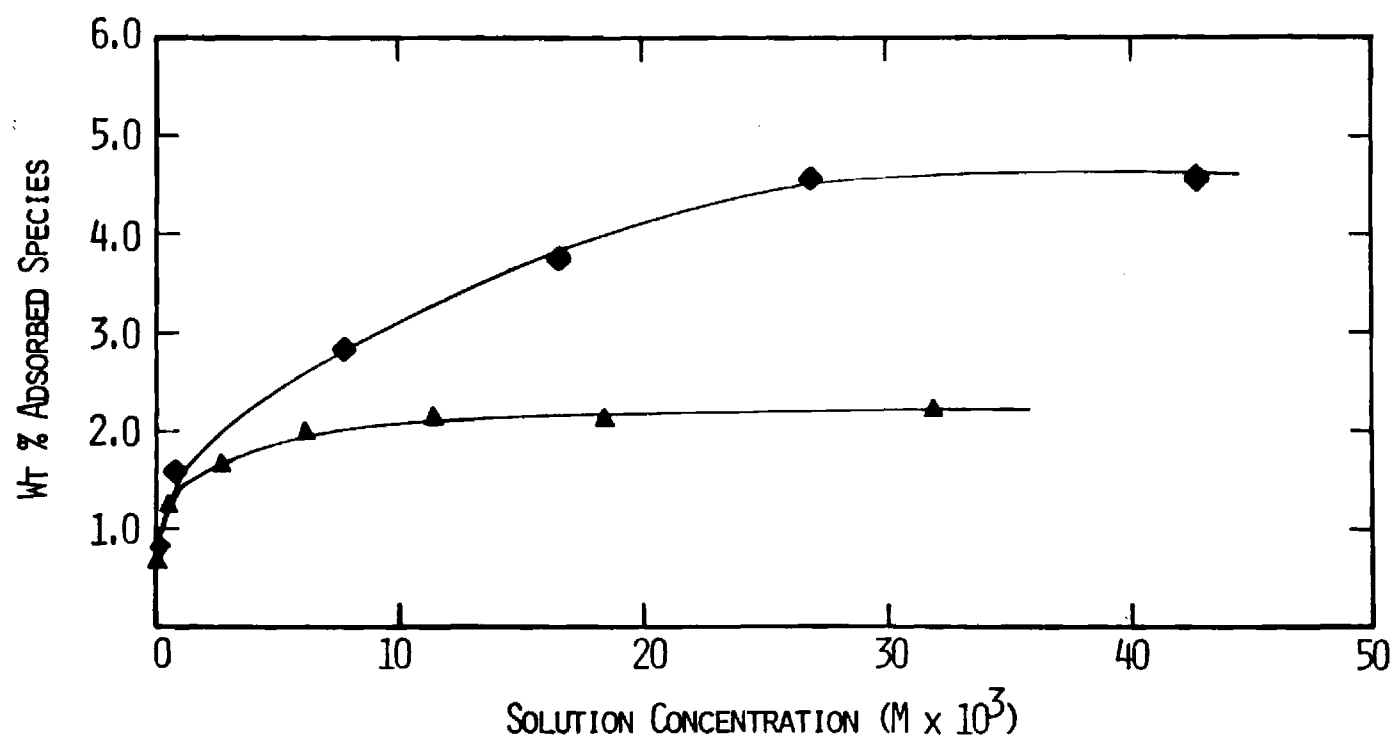


Figure 3. Adsorption isotherms (25°C) for Pt (▲) and CA (◆).

solution confirmed these expectations: after 1 hour of contact, the resulting catalyst contained a sharply defined shell of adsorbed Pt. After 22 hours of contact the Pt shell showed only slight dispersion at the inner boundary.

In most experiments the co-ingredient concentration was 0.01M, which corresponds to a co-ingredient to Pt mole ratio of 1.77. The columns in Table 1 labeled "type" refer to types of profiles which were produced in these experiments after impregnated beads had been dried and reduced. Schematic representations which most closely describe these profiles are shown in Fig. 4. These representations can be described in qualitative terms as follows:

- Type 1 -- Outer shell, sharply defined
- Type 2 -- Outer shell, diffuse
- Type 3 -- Outer shell, diffuse to center
- Type 4 -- Inner shell, sharply defined
- Type 5 -- Inner shell, diffuse
- Type 6 -- Inner shell, diffuse to center
- Type 7 -- Core, sharply defined
- Type 8 -- Core, diffuse
- Type 9 -- Linearly increasing from center

For those catalysts which have sharply defined boundaries between regions with and without Pt, such as types 1, 4 and 7, the Pt band width depended upon the co-ingredient, as shown in Table 1. With the exceptions of HF, acetic acid and tartaric acid, all co-ingredients produced sharply defined Pt profiles after 1 hour of impregnation. Of these co-ingredients only CA and tartaric acid produced an inner Pt shell, and Na citrate, a Pt core. After 22 hours of impregnation, the Pt profiles produced with AlCl_3 , HCl, NaCl, NaF, NaNO_3 , and Na Benzoate showed only slight dispersion at the inner boundaries. This finding illustrates the near irreversibility of the adsorption of Pt on alumina.

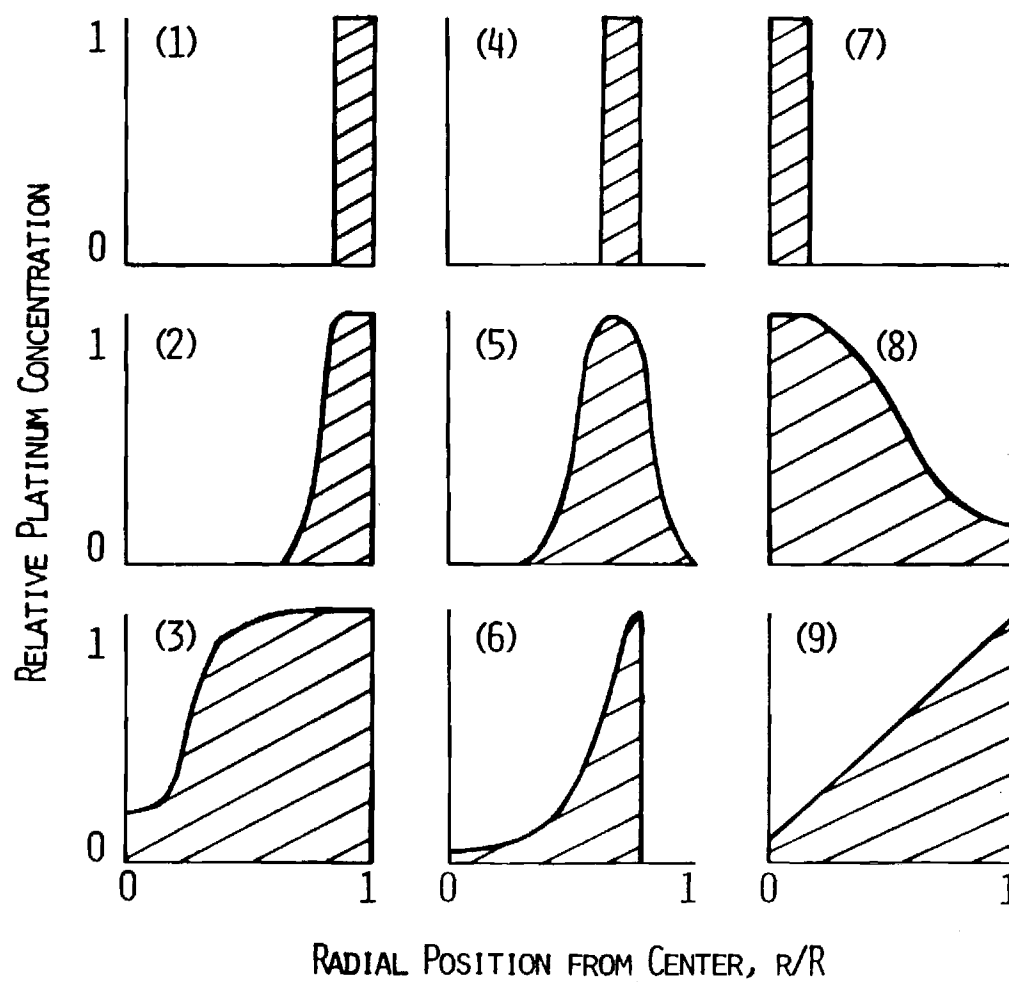


Figure 4. Types of Pt profiles obtained in co-impregnation experiments.

With the exception of catalysts prepared with co-ingredients Na_3PO_4 and Na Citrate, the weight percent of Pt in the final catalyst represented greater than 95 percent total Pt uptake from solution.

Maatman (11) discussed the roles played by competitive adsorbates in distributing Pt throughout eta-alumina supports. Michalko (13,14) showed that dibasic acids, especially CA, could be used with H_2PtCl_6 to produce shell or core profiles. Becker and Nuttall (12) studied the influence of process variables on Pt profiles when CA was used with H_2PtCl_6 . It is interesting to note that in Becker and Nuttall's work, impregnation time was an important variable -- relatively short (eg. 5 minutes) impregnation times produced sharp inner shell profiles, whereas 30 minutes impregnation time produced very diffuse almost uniform Pt profiles. Maatman (11) also reported near uniform Pt profiles after several hour impregnation times with various co-ingredients. In the present experiments, with most of the co-ingredients, impregnation time had less of an effect on Pt profiles than in previous works for reasons previously discussed. For catalysts produced with co-ingredients NaBr, HNO_3 , Na_3PO_4 , acetic acid, CA, Na Citrate, and tartaric acid, increasing the impregnation time had a significant effect on Pt profile; although only acetic acid produced a uniform Pt profile at 22 hours. Figure 5 shows an example of a profile produced by co-impregnation with NaBr for 24 hours followed by drying and reduction. Fig. 5 shows the typical data scatter that occurred in all EPM scans.

An additional series of co-impregnation experiments were run with CA at a concentration of 0.03 M and a CA to Pt mole ratio of 5.31. This concentration was used in order to produce a core instead of an inner shell. The resulting core profiles showed slight dispersion at the boundary for low impregnation times. Pt dispersion increased substantially at higher impregnation times;

however, even at times, on the order of 24 hours, profiles maintained the broad flat center which typifies a core profile (See Fig. 6).

c. Effect of NaBr on the Pt Profile

NaBr was the only co-ingredient which produced a monotonically increasing Pt profile from bead center to surface (Fig. 5). It was therefore subjected to further investigation.

Table 1 shows that NaBr had no effect on the 1 hour profile compared to the control, but had a great effect on the 22 hour profile. It appears that during the co-impregnation process, Pt adsorbed rapidly to form an outer shell catalyst; then in a comparatively slow process the NaBr interacted with the Pt or surface. This interaction increased the mobility of the Pt and allowed it to diffuse toward the center.

This simple model led to the idea of using three ingredients -- NaBr, CA, and H_2PtCl_6 -- in impregnating solution as a means of producing monotonically decreasing Pt profiles. The reasoning used was as follows: It is known that CA interacts strongly with γ -alumina (fig. 2) and successfully competes with Pt for adsorption sites to form core Pt profiles. If during the impregnation experiment, the core profile is first established and later modified by the relatively slow interaction between NaBr and adsorbed Pt, monotonically decreasing profiles might be achieved.

Fig. 7 shows that high CA concentrations can severely reduce the total uptake of Pt from aqueous solution by γ -alumina. It was therefore important in these catalyst preparation experiments, to adjust the CA to Pt ratio sufficiently high to effect a core but low enough so that high Pt uptake was maintained.

Fig. 8 shows that high NaBr concentrations can also reduce total uptake of Pt from impregnating solutions. It was therefore important in these catalyst preparation experiments to adjust the NaBr to Pt ratio high enough so that it caused the Pt profile to move but low enough so that high Pt uptake was maintained.

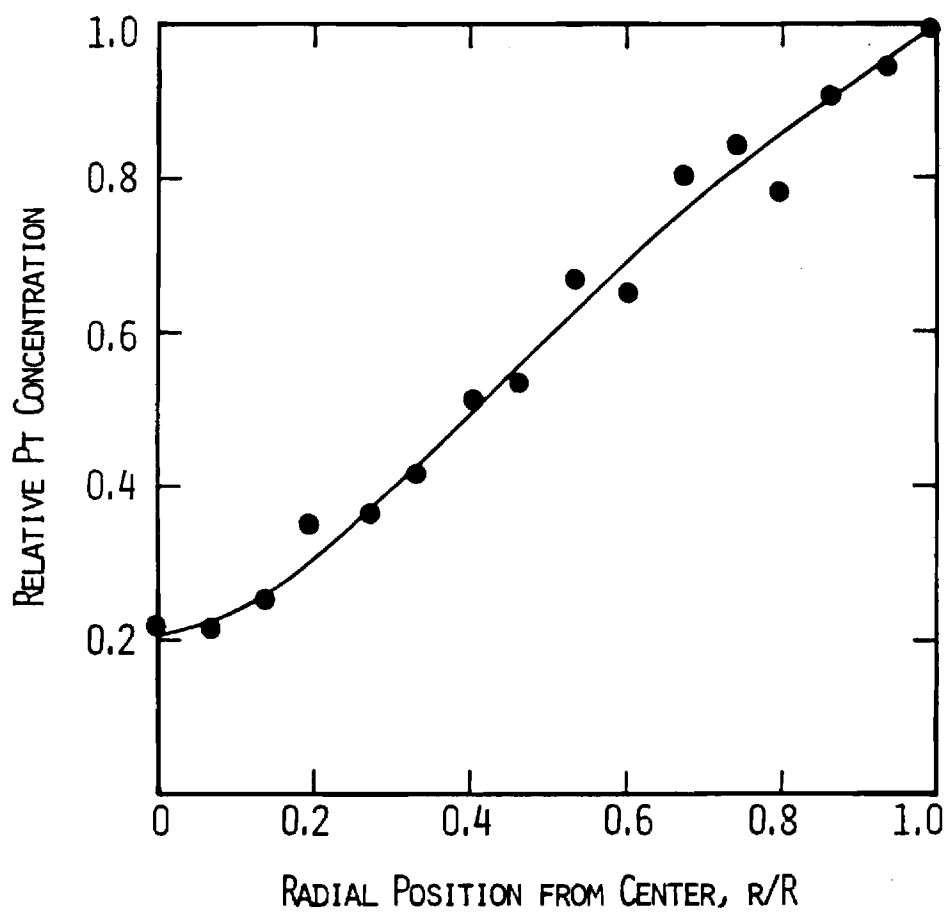


Figure 5. Pt profile produced by co-impregnation of alumina beads with NaBr and H_2PtCl_6 . Initial NaBr to Pt mole ratio = 1.77:1. Impregnation time = 24 hours. Pt content of beads = 0.50 wt%.

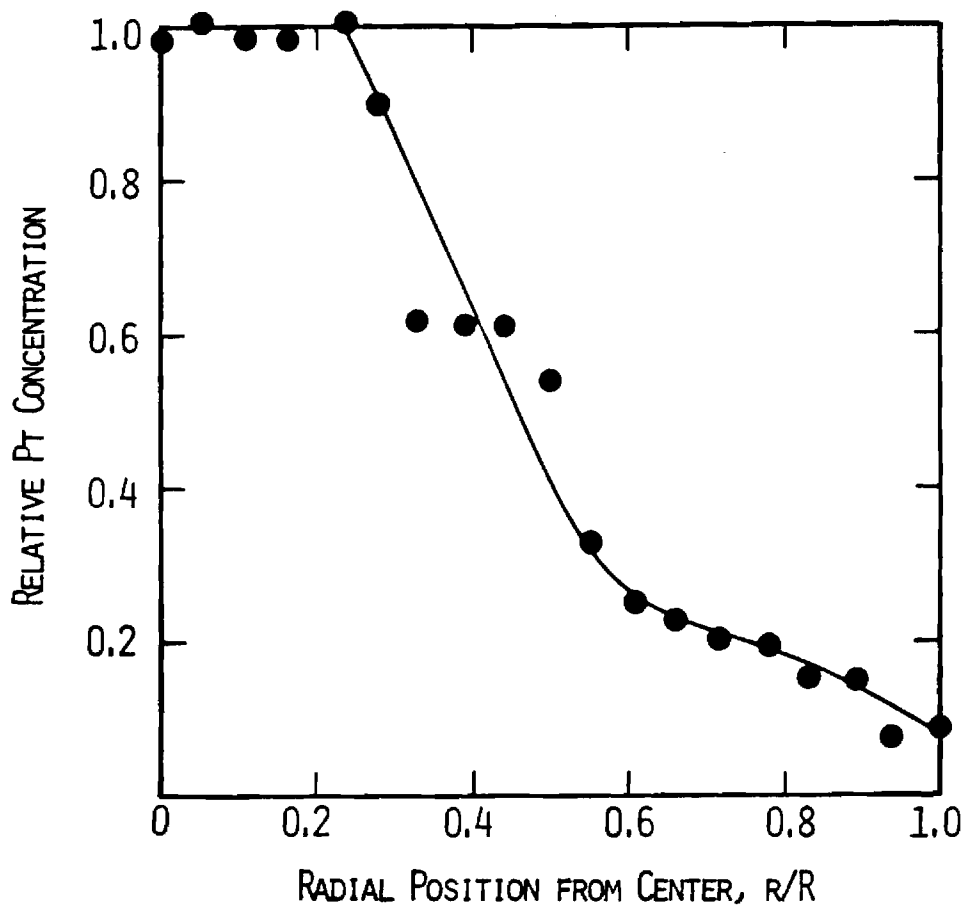


Figure 6. Core Pt profile produced by co-impregnation of γ -alumina beads with CA and H_2PtCl_6 solution. Initial CA to Pt mole ratio = 5.31:1; impregnation time = 24 hours; Pt content of beads = 0.50% .

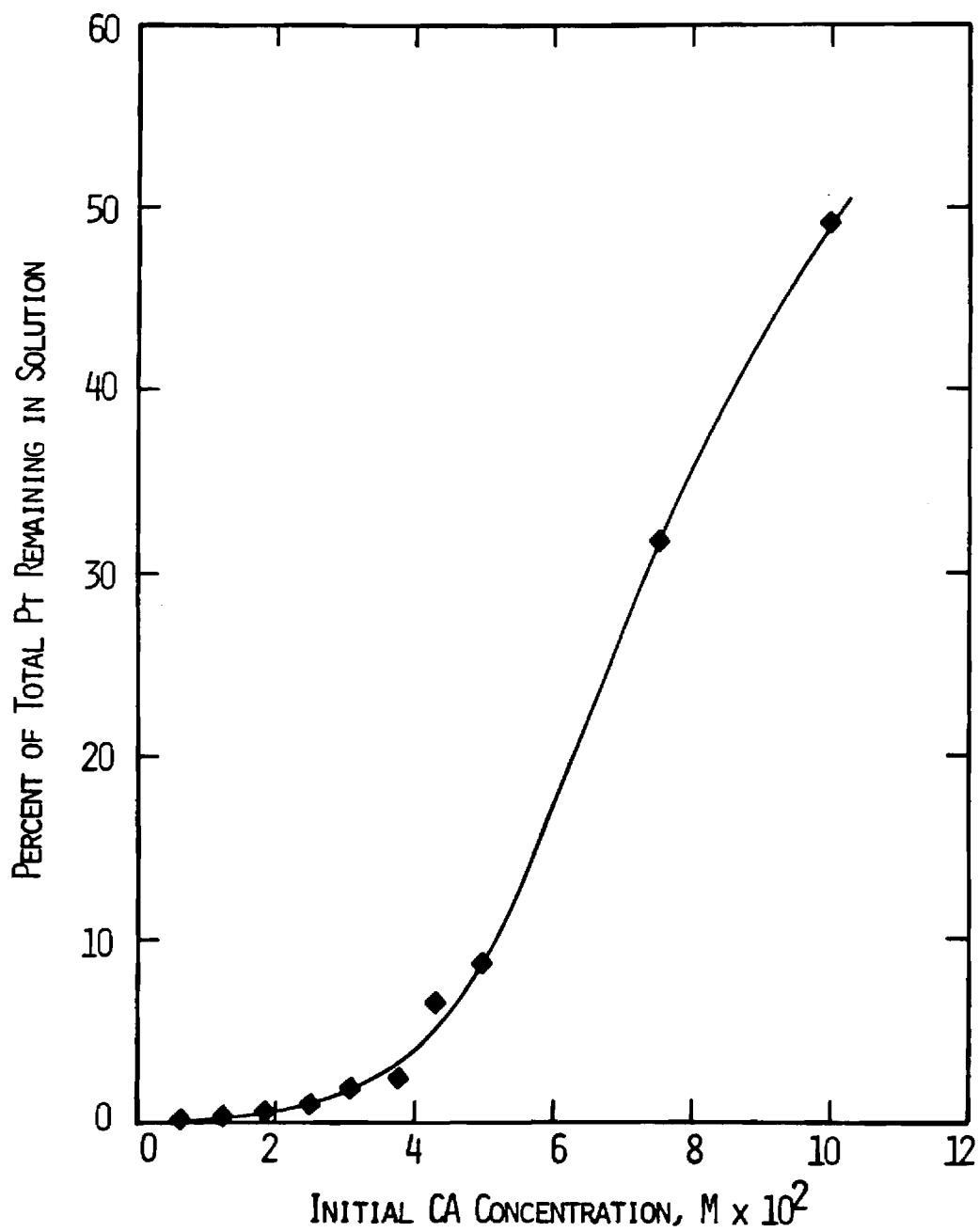


Figure 7. Effect of CA concentration on uptake of Pt from solution. Initial Pt concentration, $2.8 (10^{-3})\text{M}$; ratio of liquid volume to alumina weight, 7.5 ml/g.

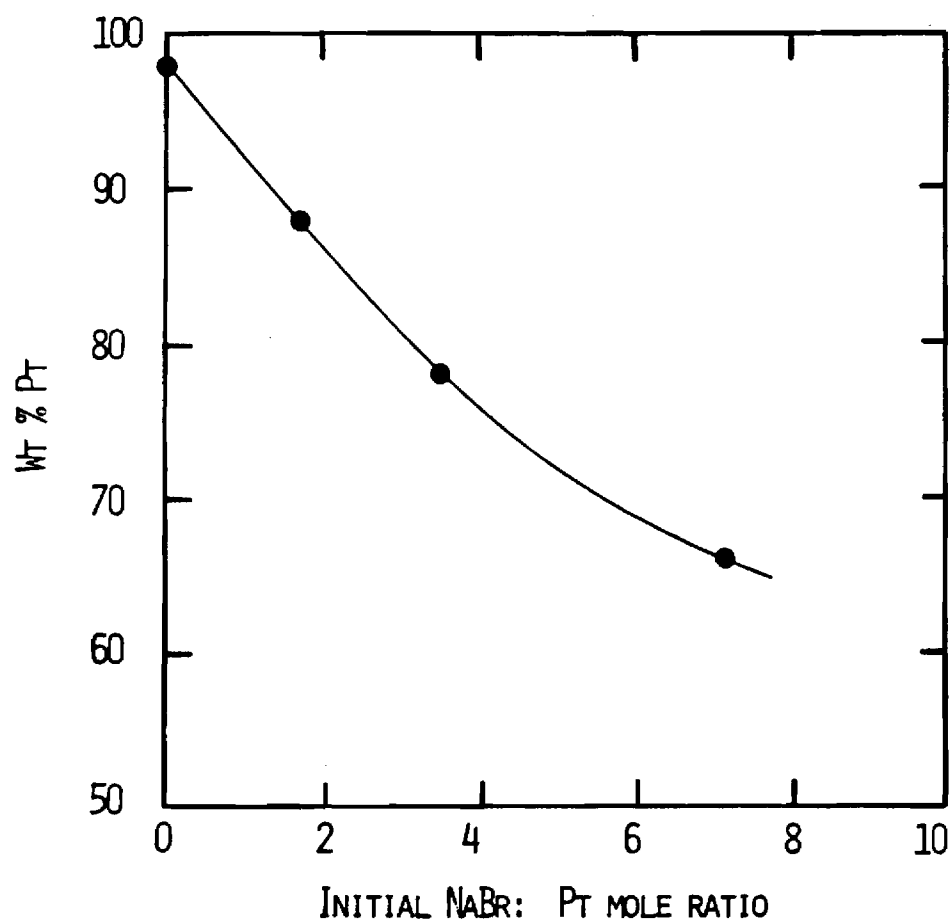


Figure 8. Effect of NaBr content on total Pt uptake by alumina beads. Initial CA:Pt mole ratio = 5.31:1. Impregnation time = 24 hours.

Fig. 9 shows the relative Pt concentration profiles for co-impregnation experiments as a function of impregnation time. For these particular experiments, the solution contained NaBr, CA, and Pt in the molar ratio 1.77: 5.31: 1. (The lines represent smooth curves drawn through the EPM data to show the data trend).

Fig. 10 shows the EPM data for the 16 hr sample. The interesting effect of the NaBr is that it produces a monotonically decreasing profile which has a sharp maximum at the bead center as opposed to a broad flat center as in Fig. 6.

Conclusions

NaBr, when used as a co-ingredient in H_2PtCl_6 or $CA-H_2PtCl_6$ impregnating solutions, is effective in modifying the Pt distribution within γ -alumina supports. Pt profiles which result from the above solutions are respectively monotonically increasing and monotonically decreasing from bead center to surface. Without the NaBr co-ingredient the above solutions produce shell and core type Pt profiles respectively. The function of the NaBr is unclear although it appears to interact with the adsorbed Pt or surface and weaken the Pt - surface bond.

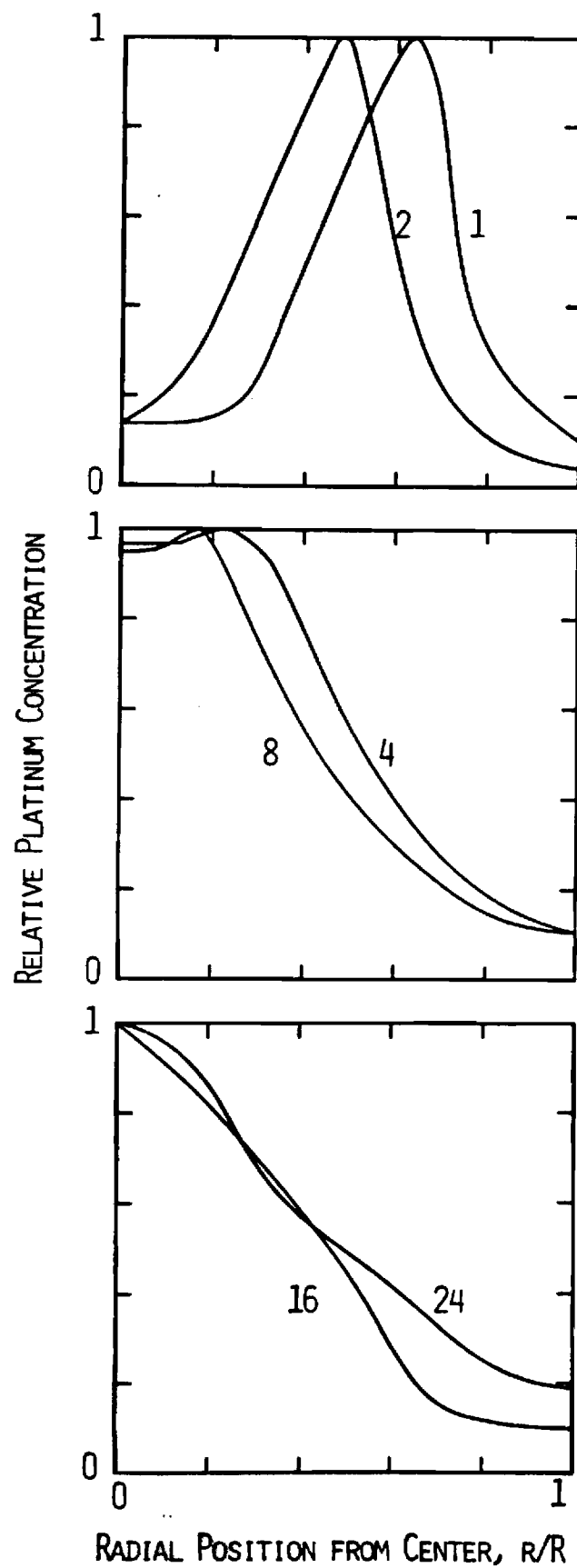


Figure 9. Effect of impregnation time on Pt profile for NaBr:CA:Pt mole ratio = 1.77:5.31:1. Impregnation times (hr) are shown on the figure.

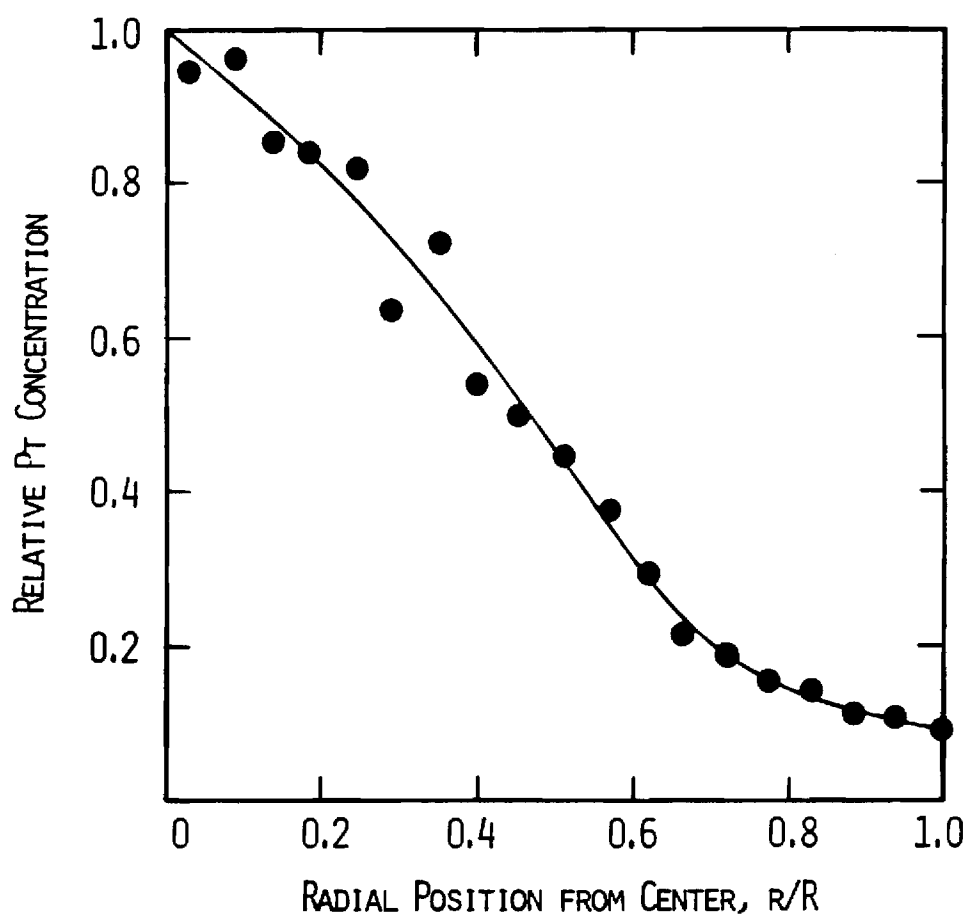


Figure 10. Pt profile produced by co-impregnation of γ -alumina beads with NaBr, CA, and H_2PtCl_6 solution. Initial NaBr:CA:Pt mole ratio = 1.77:5.31:1; impregnation time = 16 hours; Pt content of beads = 0.50%.

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FINAL PROJECT REPORT
NSF FORM 98A

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I-PROJECT IDENTIFICATION INFORMATION

1. Institution and Address Contract Administration Georgia Institute of Technology Admin. Bldg. - Atlanta, Ga. 30332	2. NSF Program Chemical Processes	3. NSF Award Number ENG 78-00731
	4. Award Period From 8/15/78 To 1/31/81	5. Cumulative Award Amount 76,932
6. Project Title An Experimental Study of the Performance of Non-Uniformly Active Catalysts.		

PART II-SUMMARY OF COMPLETED PROJECT (FOR PUBLIC USE)

The objective of this work was to experimentally study the influence of intraparticle mass transport limitation on reaction in nonuniformly active supported metal catalysts. The scope of the work involved (1) preparation of catalysts which have various radial profiles of active ingredient (2) characterization of the catalysts (3) measurement of catalytic activity and selectivity and (4) comparison of experimental reaction data with published model predictions.

Techniques used in the study included (1) preparation of supported Pt on γ -alumina by impregnation (2) characterization of the catalysts by H_2 - chemisorption, x-ray line broadening, x-ray fluorescence, electron probe microanalysis and transmission electron microscopy, and (3) reaction in a well stirred batch single bead reactor; the reaction system involved the deuterium-neopentane exchange reaction on Pt.

A novel, reproducible, technique for preparing nonuniformly active Pt catalysts has been developed. Catalysts with monotonically increasing and decreasing radial Pt profiles have been prepared. The new approach involves adding NaBr to the impregnating solution. These catalysts have been well characterized by the techniques listed above, and have been studied in reaction experiments. The reaction data at low temperature could be fit by a model which describes the influence of diffusion on reaction. At higher temperature the data could be described by a two parameter model which describes the influence of diffusion and desorption effects on reaction. Reaction studies on crushed catalysts showed that the deuterium-neopentane exchange reaction on supported Pt is independent of Pt dispersion.

PART III-TECHNICAL INFORMATION (FOR PROGRAM MANAGEMENT USES)

1. ITEM (Check appropriate blocks)	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses					
b. Publication Citations		X			
c. Data on Scientific Collaborators		X			
d. Information on Inventions		X			
e. Technical Description of Project and Results		X	X		
f. Other (specify)					
2. Principal Investigator/Project Director Name (Typed) William R. Ernst	3. Principal Investigator/Project Director Signature			4. Date 4/1/81	

III 1. A

**PREPARATION, CHARACTERIZATION AND PERFORMANCE OF
NON-UNIFORM METAL CATALYSTS**

A DISSERTATION

Presented to

The Faculty of the Division of Graduate Studies

By

Yen-Shin Shyr

**In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
in the School of Chemical Engineering**

Georgia Institute of Technology

December, 1980

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SUMMARY

Non-uniformly distributed supported Pt catalyst can be prepared by adding NaBr, and/or CA to chloroplatinic acid impregnating solution. The effect of chemical competitors in the adsorption of the impregnation process was studied. Coingredients included the following acids and salts: HCl, HF, HNO₃, acetic acid, citric acid, tartaric acid, AlCl₃, NaCl, NaF, NaBr, NaNO₃, NaPO₄, Na benzoate, and Na citrate.

Radial Pt profiles were analyzed by electron probe microanalysis. Five catalysts — two with monotonically increasing profiles from bead center to surface, two with monotonically decreasing profiles and one with a uniform profile on the γ -alumina support, and two catalysts — one with an increasing profile and one with a uniform profile on silica-alumina support, were prepared and characterized by EPM, and hydrogen chemisorption. The Pt contents ranged from 0.5% to 1.1% as measured by a spectrophotometric method. The Pt particle sizes were determined by H₂ chemisorption.

Neopentane-deuterium exchange reaction was used to test the performance of these catalysts. Two previously developed kinetic reaction models were used to simulate the reaction system. The one parameter model, which contains the Thiele modulus, ϕ_1 , predicted the reaction data at temperatures below 200°C. The two parameter model, which contains the Thiele modulus, ϕ_1 and desorption parameter, θ , predicted reaction data at temperatures between 200 and 250°C. Neither the one parameter model nor the two parameter model explained the reaction data at temperatures above

250°C. The activation energy of these reactions on the supported Pt catalyst is equal to 30 ± 2 kcal/gmole.

Multiple exchange reaction model was tried to improve the fit between data and models. Different criteria functions were also used to do the optimization in the model simulation. There is no significant improvement through these approaches.

The methods used to calculate the effectiveness factor of the reaction included analytical solutions to special distribution profiles and the numerical orthogonal collocation method. For the first order reaction the effectiveness factor is higher for the active metal concentrated in the outer shell area of bead at a given ϕ_1 .

The selectivity of the neopentane-deuterium exchange reaction was derived both by theoretical calculation and experimental work. The selectivity to highly deuterated compounds is greatest for those catalysts having decreasing activity profile from the bead center to the surface. The selectivity is lower for those catalysts having increasing activity profile from the bead center to the surface.

Preparation of Nonuniformly Active Catalysts

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Received September 27, 1979

The effect of adding chemical coingredients to H_2PtCl_6 impregnating solutions in order to modify Pt profiles in spherical γ -alumina beads was studied. Coingredients included the following acids and salts: HCl, HF, HNO_3 , acetic acid, citric acid, tartaric, $AlCl_3$, NaCl, NaF, NaBr, $NaNO_3$, Na_3PO_4 , Na benzoate, and Na citrate. Radial Pt profiles were examined by electron probe microanalysis of bead cross sections. Nine distinctly different types of profiles were produced. NaBr was the only coingredient which produced a monotonically increasing Pt profile from bead center to surface. A simple model which describes the role of NaBr during the impregnation process was discussed. A method of producing monotonically decreasing Pt profiles from bead center to surface which involves incorporating both NaBr and citric acid in H_2PtCl_6 impregnating solution was studied.

INTRODUCTION

Nonuniformity of activity in supported metal catalysts can occur as a result of catalyst preparation methods or catalyst poisoning. Nonuniformly active catalysts may in some processes exhibit superior activity, selectivity, or resistance to poisoning compared to uniformly active catalysts. Many recent papers have discussed theories of diffusion and reaction in nonuniformly active catalysts (1-6). Less attention has been focused on fundamental experimental studies which involve preparation, characterization, and evaluation of performance in kinetic studies involving probe reactions. Several challenging questions arise when one attempts such fundamental studies; e.g., what parameters should be adjusted during catalyst preparation in order to produce a desired distribution of active ingredient within a support particle? Quantitative measurement of mass distribution of active ingredient within a particle can easily be determined for metals by electron probe microanalysis, but how does one quantitatively measure "activity" distribution within a particle? Is

it valid to assume constant diffusivity throughout a nonuniformly active catalyst particle, as often assumed in published models? Experimental verification of model predictions is necessary if one is to have confidence in these models as tools for design.

A recent paper presented the theoretical basis for a kinetic study to determine the effect of activity distribution in spherical catalyst particles on selectivity of the deuterium-hydride exchange reaction (7). The catalyst considered was alumina-supported platinum. (This reaction was shown previously to be a suitable probe for diffusional influences in uniformly active catalysts (8, 9)). This paper presents results of the catalyst preparation phase of this study. A later article will report results of characterization and kinetic studies.

Impregnation was selected as the means of preparing the catalysts because of its simplicity and wide use. Previous workers have developed ways of producing uniform profiles of active ingredient (e.g., (10, 11)) and sharply defined profiles such as outer shells, inner shells, and cores (e.g., (12-14)). Workers have investigated many preparation variables and their influence on the distribution of active ingredient in a number

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of metal-support combinations (11, 15-18). There exists a broad body of knowledge of the physical and chemical processes of the impregnation process and surface chemistry of support materials (e.g., (19-28)). However, each metal-support combination is unique and hence introduces new challenges to the investigator.

An objective of this work was to investigate the possibility of using chemical additives (coingredients) in impregnating solutions as a means of controlling the distribution of active ingredient within the catalyst particle. Platinum on spherical γ -alumina beads was the system studied. Of particular interest for our future kinetic studies would be the ability to approximately reproduce some of the profiles that are considered in theoretical studies previously mentioned (3-6)—e.g., profiles which monotonically increase or decrease from particle center to surface. Linearly increasing or decreasing profiles were frequently considered in these theoretical studies.

Catalysts which have monotonically decreasing profiles are of some interest in kinetic studies because they serve as models of partially poisoned catalysts. There may also be commercial interest in such catalysts especially for reactions which are diffusion limited and in which the catalyst undergoes a shell progressive poisoning. They may exhibit activity or poisoning resistance that is superior to uniform or shell profiles.

Hexachloroplatinic acid was the active ingredient selected for this study. The strong interaction between H_2PtCl_6 and γ -alumina is known to produce shell catalysts which have a well-defined boundary between Pt and bare support. Citric acid was employed as an additive to the H_2PtCl_6 solution because this combination is known to produce core catalysts. The approach that was used to find a means of controlling Pt profile was: first, to explore the interactions of H_2PtCl_6 and citric acid with the alumina supports; second, to experimen-

tally survey a large number of chemical additives which, when included in the impregnating solutions, modify the shell or core profile; and third, to select and further investigate the chemical additive which yields the Pt profiles desired.

EXPERIMENTAL METHODS

A 0.0564 M stock solution of H_2PtCl_6 was prepared by dissolving Fisher Certified $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in deionized and carbon-treated water. Solution concentrations were determined by a spectrophotometric method (29) on a Bausch and Lomb spectrophotometer. Concentrations were expressed as moles of Pt per liter. A 0.1 M stock solution of citric acid (CA) was prepared from Fisher Certified CA. Solution concentrations were determined by titration. Stock solutions of various acids or salts (Table 1) were prepared to give concentrations of about 0.1 M. γ -Alumina beads of spherical geometry (Rhône Poulenc Inc., GOD-30) had the following properties: diameter, 0.36 cm; bulk density, 0.3 g/cm³; surface area, 150 m²/g; total pore volume, 1.70 cm³/g; and average pore diameter, 450 Å.

Adsorption isotherm experiments involved contacting eight alumina beads (ca. 0.1 g) with 0.5 cm³ of solution containing CA or H_2PtCl_6 at 25°C. All solutions were prepared by diluting the stock solutions described above. After 2 hr of contacting, beads were separated from solution by filtration and washed with 2 cm³ of water to quantitatively remove and recover external solution. Washing time and volume were kept to a minimum to avoid removal of active ingredient from pore solution. The recovered solution was diluted with water to a volume of 5 cm³ and analyzed for active ingredient. The amount of adsorption was determined by the difference between initial and final concentrations of active ingredient in solution after correcting for pore volume.

In experiments designed to test a large number of acids and salts as coimpregnat-

ing ingredients, solutions were prepared by adding stock solutions of H_2PtCl_6 , acid or salt solution, and water in the volumetric ratio 1:1:8. The experimental procedure involved placing eight alumina beads in contact with 0.5 cm^3 of impregnating solution for 1 or 22 hr at 25°C . The beads were removed from solution, washed with 2 cm^3 of water, dried in air at 120°C for 8 hr, and reduced in flowing H_2 at 500°C for 1 hr. Residual impregnating solution combined with wash water was analyzed for Pt. Characterization as to the type of Pt profile was determined by visual observation or by electron probe microanalysis (EPM) of beads that had been cleaved in half (30). EPM was performed on an Acton MS-64 microprobe using a point count technique. Beads that had been cleaved in half were scanned across the flat side through the bead center. Thirty-second counts were taken at $100\text{-}\mu\text{m}$ intervals across the surface. Scans at one to four orientations were taken for each bead. Data smoothing consisted of averaging the scan data taken at all orientations and reporting the averaged and normalized Pt profile from bead center ($r/R = 0$) to surface ($r/R = 1$). Visual observation was used when the profile was obviously a shell or core type with a sharp boundary between Pt and bare support. EPM was used when the profile was diffuse.

More extensive coimpregnation studies using solutions prepared from various combinations of H_2PtCl_6 , CA and NaBr stock solutions, and water of dilution were conducted in a manner similar to the above experiments; however, in the more extensive studies, the effects of impregnation time and NaBr and CA concentrations on final Pt profile were studied. EPM was used in determining Pt profiles for all samples.

RESULTS AND DISCUSSION

a. Adsorption Studies

Adsorption plays a large role in the impregnation of γ -alumina with H_2PtCl_6 solu-

tion. The bonding between Pt complex (henceforth referred to as Pt) and the surface is not well understood although mechanisms have been suggested. For example, recent studies have suggested that the adsorption of Pt is associated with either (1) variation of pH of the solution due to acid attack of the alumina with dissolution of surface aluminum ions (25), or (2) ligand displacement reaction of anionic Pt complexes with the alumina surface (27).

Figure 1 shows the total uptake of Pt after beads were contacted for 2 hr with impregnating solution containing H_2PtCl_6 , then washed, dried, and reduced. The ordinate of this graph, "total Pt uptake," takes into account both adsorbed Pt and Pt deposited from pore solution during drying. The solid line shows the trend of the data. The dashed 45° line is a theoretical line for irreversible adsorption. The fact that data points at initial Pt values of about 0.006 mole and below fall near the theoretical line shows the strong interaction between Pt and γ -alumina. The other dashed line shows the trend of data at large values of initial Pt. The increase in the total Pt uptake in this linear region is due to Pt deposited from pore solution during drying. This increase can be used to determine the effective pore volume for the Pt in solution (21, 31, 32). The intersection of the two dashed lines represents the Pt uptake at saturation coverage of adsorption sites. The saturation coverage, 0.012 mmole Pt,

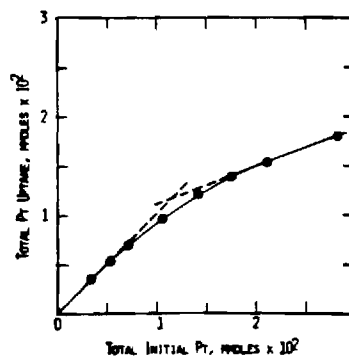


FIG. 1. Total uptake of Pt from impregnating solution by γ -alumina.

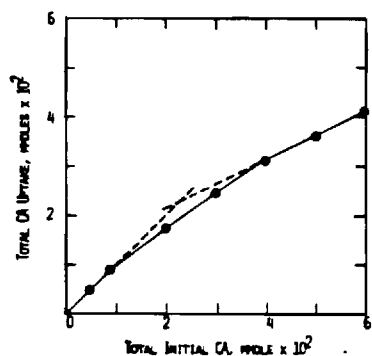


FIG. 2. Total uptake of CA from impregnating solution by γ -alumina.

divided by alumina sample weight and surface area corresponds to 110 $\mu\text{mole/g}$ and 750 $\mu\text{mole/m}^2$, respectively.

Figure 2 is a similar graph for the total uptake of CA. As in the case of Pt, data points at low initial CA fall near the dashed 45° line thus showing a strong interaction between CA and γ -alumina; at large initial CA the data trend is linear. Intersection of the two dashed lines, which corresponds to saturation coverage of adsorption sites, oc-

curs at 0.023 mmole CA. Saturation coverage divided by sample weight and surface area equals 215 $\mu\text{mole/g}$ and 1433 $\mu\text{mole/m}^2$, respectively, or approximately twice the saturation coverage for Pt.

Adsorption isotherms (Fig. 3) were determined for both Pt and CA from data in Figs. 1 and 2 by subtracting the effective pore volume contribution from total uptake. The isotherms are expressed in terms of percent of adsorbed species. The line through the Pt data corresponds to the Langmuir equation:

$$\text{wt\% Pt} = \frac{2880C}{1 + 1330C}$$

The CA data do not conform to the Langmuir model. A line was drawn, however, to show the trend of the data.

b. Effect of Coingredients on Pt Profile

Table 1 presents a list of acids and salts which were studied in a set of coimpregnation experiments. The purpose was to screen a large number of chemicals as coingredients with H_2PtCl_6 to determine their

TABLE I
Properties of Coimpregnated Catalysts

Acid or salt	Impregnation time, 1 hr					Impregnation time, 22 hr		
	Conc (M)	Pt (wt%)	Pt band, r/R			Conc (M)	Pt (wt%)	Pt band
			Begins at	Ends at	Type			
None	—	0.51	1	0.77	1	—	0.51	2
AlCl_3	0.01	0.50	1	0.56	1	0.01	0.51	2
HCl	0.01	0.51	1	0.67	1	0.01	0.50	2
NaCl	0.01	0.49	1	0.81	1	0.01	0.51	2
HF	0.01	0.50	—	—	5	0.01	0.50	5
NaF	0.01	0.51	1	0.83	1	0.01	0.51	2
NaBr	0.01	0.50	1	0.77	1	0.01	0.50	9
HNO_3	0.01	0.50	1	0.50	1	0.01	0.51	3
NaNO_3	0.008	0.49	1	0.79	1	0.008	0.51	2
Na_3PO_4^*	0.01	0.31	0.83	0	7	0.01	0.10	8
Na benzoate	0.01	0.48	1	0.78	1	0.01	0.50	2
Acetic acid	0.01	0.51	—	—	3	0.01	0.50	uniform
Citric acid	0.01	0.49	0.84	0.44	4	0.01	0.48	6
Na citrate*	0.02	0.19	0.33	0	7	0.01	0.14	8
Tartaric acid	0.01	0.49	—	—	6	0.01	0.51	7

* The 22-hr sample was prepared using a fresh solution of Na_3PO_4 (or Na citrate) and H_2PtCl_6 while the 1-hr sample was prepared using a portion of that same solution after it had been stored for 2 or 3 days.

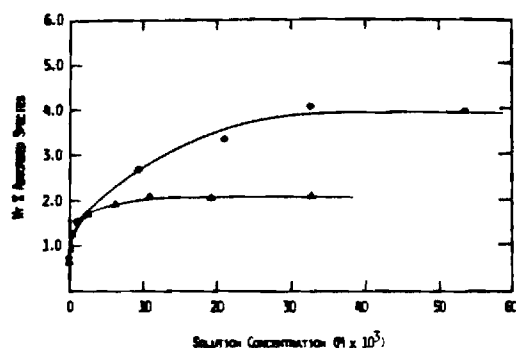


FIG. 3. Adsorption isotherms (25°C) for Pt (▲) and CA (◆).

effects upon the final Pt profile in the alumina beads. It was desirable to examine these effects after relatively short (1 hr) and long (22 hr) impregnation times, and to eliminate profile changes over this time period due to Pt diffusing into the pores from external impregnating solution. To avoid this undesirable effect, the total amount of Pt and total volume of solution were kept low—total Pt in solution was about 23% of the amount required to saturate the adsorption sites in the alumina (Fig. 1); solution volume was about 2.7 times the pore volume. Under these conditions, at short impregnation time, the solution would become essentially depleted of Pt as the Pt adsorbed on the support thus substantially reducing any driving force for diffusion. A control experiment in which no coingredient (Table 1, first entry) was added to the solution confirmed these expectations: after 1 hr of contact, the resulting catalyst contained a sharply defined shell of adsorbed Pt. After 22 hr of contact, the Pt shell showed only slight dispersion at the inner boundary.

In most experiments the coingredient concentration was 0.01 *M*, which corresponds to a coingredient to Pt mole ratio of 1.77. The columns in Table 1 labeled "type" refer to types of profiles which were produced in these experiments after impregnated beads had been dried and reduced. Schematic representations which

most closely describe these profiles are shown in Fig. 4. These representations can be described in qualitative terms as follows:

- Type 1—Outer shell, sharply defined
- Type 2—Outer shell, diffuse
- Type 3—Outer shell, diffuse to center
- Type 4—Inner shell, sharply defined
- Type 5—Inner shell, diffuse
- Type 6—Inner shell, diffuse to center
- Type 7—Core, sharply defined
- Type 8—Core, diffuse
- Type 9—Linearly increasing from center

For those catalysts which have sharply defined boundaries between regions with and without Pt, such as types 1, 4, and 7, the Pt bandwidth depended upon the coingredient, as shown in Table 1. With the exceptions of HF, acetic acid, and tartaric acid, all coingredients produced sharply defined Pt profiles after 1 hr of impregnation. Of these coingredients only CA and tartaric acid produced an inner Pt shell, and Na citrate, a Pt core. After 22 hr of impregnation, the Pt profiles produced with AlCl_3 , HCl, NaCl, NaF, NaNO_3 , and Na benzoate showed only slight dispersion at the inner boundaries. This finding illustrates the near irreversibility of the adsorption of Pt on alumina. With the exception of catalysts prepared with coingredients Na_3PO_4 and Na citrate, the weight percent of Pt in the

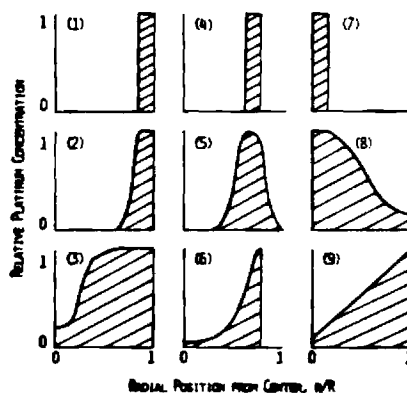


FIG. 4. Types of Pt profiles obtained in coimpregnation experiments.

final catalyst represented greater than 95% total Pt uptake from solution.

Maatman (11) discussed the roles played by competitive adsorbates in distributing Pt throughout γ -alumina supports. Michalko (13, 14) showed that dibasic acids, especially CA, could be used with H_2PtCl_6 to produce shell or core profiles. Becker and Nuttall (12) studied the influence of process variables on Pt profiles when CA was used with H_2PtCl_6 . It is interesting to note that in Becker and Nuttall's work, impregnation time was an important variable—relatively short (e.g., 5 min) impregnation times produced sharp inner shell profiles, whereas 30-min impregnation time produced very diffuse almost uniform Pt profiles. Maatman (11) also reported near uniform Pt profiles after several-hour impregnation times with various coingredients. In the present experiments, with most of the coingredients, impregnation time had less of an effect on Pt profiles than in previous works for reasons previously discussed. For catalysts produced with coingredients NaBr, HNO_3 , Na_3PO_4 , acetic acid, CA, Na citrate, and tartaric acid, increasing the impregnation time had a significant effect on Pt profile, although only acetic acid produced a uniform Pt profile at 22 hr. Figure 5 shows an example of a profile produced by coimpregnation with NaBr for 24 hr followed by drying and reduction. Figure 5

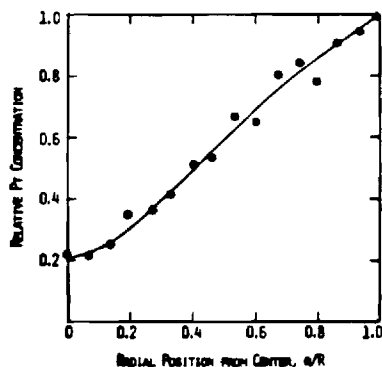


FIG. 5. Pt profile produced by coimpregnation of alumina beads with NaBr and H_2PtCl_6 . Initial NaBr:Pt mole ratio, 1.77:1; impregnation time, 24 hr; Pt content of beads, 0.50 wt%.

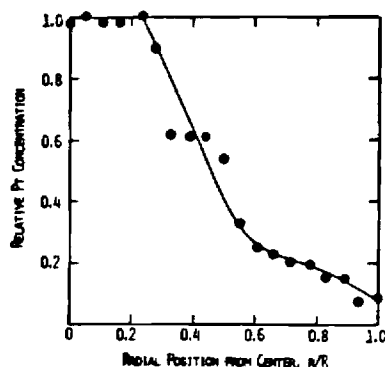


FIG. 6. Core Pt profile produced by coimpregnation of γ -alumina beads with CA and H_2PtCl_6 solution. Initial CA:Pt molar ratio, 5.31:1; impregnation time, 24 hr; Pt content of beads, 0.50 wt%.

shows the typical data scatter that occurred in all EPM scans.

An additional series of coimpregnation experiments were run with CA at a concentration of 0.03 M and a CA to Pt mole ratio of 5.31. This concentration was used in order to produce a core instead of an inner shell. The resulting core profiles showed slight dispersion at the boundary for low impregnation times. Pt dispersion increased substantially at higher impregnation times; however, even at times on the order of 24 hr, profiles maintained the broad flat center which typifies a core profile (see Fig. 6).

c. Effect of NaBr on the Pt Profile

NaBr was the only coingredient which produced a monotonically increasing Pt profile from bead center to surface (Fig. 5). It was therefore subjected to further investigation.

Table 1 shows that NaBr had no effect on the 1-hr profile compared to the control, but had a great effect on the 22-hr profile. It appears that during the coimpregnation process, Pt adsorbed rapidly to form an outer shell catalyst; then in a comparatively slow process the NaBr interacted with the Pt or surface. This interaction increased the mobility of the Pt and allowed it to diffuse toward the center.

This simple model led to the idea of using three ingredients—NaBr, CA, and

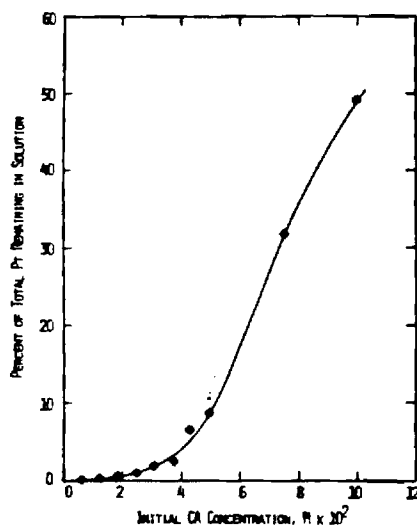


FIG. 7. Effect of CA concentration on uptake of Pt from solution. Initial Pt concentration, $2.8 \times 10^{-3} M$; ratio of liquid volume to alumina weight, 7.5 ml/g.

H_2PtCl_6 —in impregnating solution as a means of producing monotonically decreasing Pt profiles. The reasoning used was as follows: It is known that CA interacts strongly with γ -alumina (Fig. 2) and successfully competes with Pt for adsorption sites to form core Pt profiles. If during the impregnation experiment, the core profile is first established and later modified by the relatively slow interaction between NaBr and adsorbed Pt, monotonically decreasing profiles might be achieved.

Figure 7 shows that high CA concentrations can severely reduce the total uptake

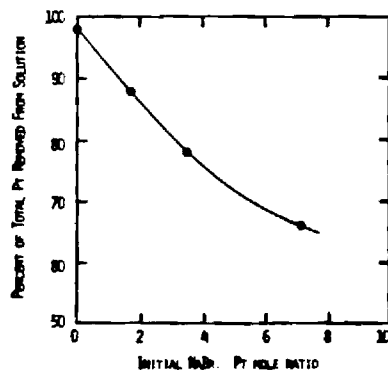


FIG. 8. Effect of NaBr content on total Pt uptake by alumina beads. Initial CA:Pt mole ratio, 5.31:1; impregnation time, 24 hr.

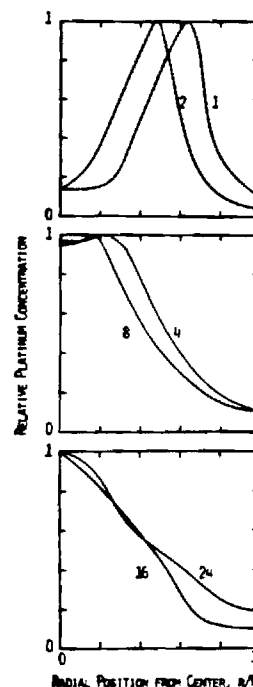


FIG. 9. Effect of impregnation on Pt profile for NaBr:CA:Pt mole ratio 1.77:5.31:1. Impregnation times (hr) are shown on the figure.

of Pt from aqueous solution by γ -alumina. It was therefore important in these catalyst preparation experiments to adjust the CA to Pt ratio sufficiently high to effect a core but low enough so that high Pt uptake was maintained.

Figure 8 shows that high NaBr concentrations can also reduce total uptake of Pt from impregnating solutions. It was therefore important in these catalyst preparation experiments to adjust the NaBr to Pt ratio high enough so that it caused the Pt profile to move but low enough so that high Pt uptake was maintained.

Figure 9 shows the relative Pt concentration profiles for coimpregnation experiments as a function of impregnation time. For these particular experiments, the solution contained NaBr, CA, and Pt in the molar ratio 1.77:5.31:1. (The lines represent smooth curves drawn through the EPM data to show the data trend.)

Figure 10 shows the EPM data for the 16-

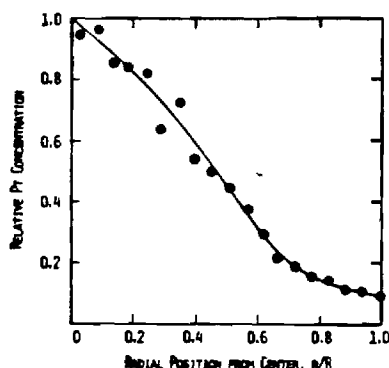


FIG. 10. Pt profile produced by coimpregnation of γ -alumina beads with NaBr, CA, and H_2PtCl_6 solution. Initial NaBr: CA: Pt mole ratio, 1.77:5.31:1; impregnation time, 16 hr; Pt content of beads, 0.50%.

hr sample. The interesting effect of the NaBr is that it produces a monotonically decreasing profile which has a sharp maximum at the bead center as opposed to a broad flat center as in Fig. 6.

CONCLUSIONS

NaBr, when used as a coingredient in H_2PtCl_6 or CA- H_2PtCl_6 impregnating solutions, is effective in modifying the Pt distribution within γ -alumina supports. Pt profiles which result from the above solutions are respectively monotonically increasing and monotonically decreasing from bead center to surface. Without the NaBr coingredient the above solutions produce shell- and core-type Pt profiles respectively. The function of the NaBr is unclear although it appears to interact with the adsorbed Pt or surface and weaken the Pt-surface bond.

ACKNOWLEDGMENTS

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III. 1. C -- Scientific Collaborators

(1) Graduate students

(a) Yen-Shin Shyr, PhD 1980

(b) Gunseli Sagun, PhD candidate

III. 1. D -- Inventions/Patents

A Record of Invention entitled "Method of Preparing Nonuniformly Active Catalysts" was filed at Georgia Tech by co-inventors William R. Ernst and Yen-Shin Shyr on 9/19/79; a preliminary patentability search on the invention was performed by the law firm of Newton, Hopkins and Ormsby in Atlanta. The patent application is currently being prepared.

III. 1. E

A. The following information is attached.

(1) Final Report for ENG 78-00731

(2) Yr. 2 Report: Progress Report for ENG 78-00731 for the Period 8/15/79 to 8/15/80.

B. The following information was previously furnished.

(1) Yr. 1 Report: Progress Report for ENG 78-00731 for the Period 8/15/78 to 8/15/79.

III 1 E
A(1)

FINAL REPORT FOR

ENG 78-00731

SUMMARY OF PROGRESS TO DATE

Table 1 contains the four primary objectives of the overall program (ENG 78-00731 and currently funded CPE 80 - 05713), and the major goals that must be achieved in order to satisfy each primary objective. Table 2 is a time schedule for the overall program duration which summarizes progress made on each of the goals during the two years (8/15/78 to 8/15/80) of ENG 78-00731, and anticipated progress to the end of currently funded CPE 80-05713 (10/15/82). Numbers in Table 2 are estimates of percentages of total work still to be completed as of the date indicated. (100% means work not begun; 0% means goal accomplished). Goals no's II-F, III-F, IV-C and IV-E were not originally proposed in ENG 78-00731, but were conceived after ENG-78-00731 funded as work that would strengthen the overall program. Work began on these four latter goals during the second year of ENG 78-00731.

It should be noted that some of the goals listed in our original proposal--numbers II-E, III-C, III-D, III-E, were not accomplished during the funded period of ENG 78-00731. This is due to the fact that our original proposal was for three years duration; funding from NSF, however, was for the first two years of the proposal. We expect to complete these latter goals during CPE 80-05713.

Major achievements made between 8/15/78 and 8/15/80 are discussed in detail in annual reports. The following is a listing which summarizes these achievements.

1. All equipment items for catalyst preparation, catalyst characterization, and reaction experiments have been procured, erected and tested. Two different reactor types were built and interfaced with a mass spectrometer -- a stirred batch reactor and a batch reactor with gas re-circulation pump.

2. A novel, reproducible, technique has been developed for preparing catalysts with monotonically increasing or decreasing concentration profiles of Pt from particle center to external surface. The starting point in the development of the technique was a previously patented technique for producing core, inner and outer shell profiles. The new approach involves the addition of NaBr to the impregnation solution.
3. An article which discusses the above catalyst preparation method was published (1).
4. Seven nonuniformly active catalysts with different type Pt profiles have been prepared and characterized for total Pt content, average Pt crystallite size, total Pt surface area and radial distribution of Pt content respectively by a spectrophotometric method (and x-ray fluorescence), H_2 chemisorption and electron probe microanalysis.
5. A diffusion cell based on the technique of Gorring and deRosset (2) was constructed and tested. Diffusion coefficients determined by this method agreed with results of Wicke-Kallenbach tests on the same beads to within 30 percent.
6. A total of forty-three deuterium-neopentane exchange experiments on single well characterized catalyst particles mentioned in 4 above have been run in a well stirred batch reactor. Reaction temperatures ranged from 150 to 280°C. Reaction temperature was the variable used to adjust Thiele modulus. The data from experiments conducted at low temperatures could be fit by a one parameter model which describes diffusion and reaction in a catalyst sphere. A two parameter model which takes into account both diffusion and desorption effects on reaction fit the data more closely over the entire temperature range of the experiments. Contrary to our original expectations, desorption

influences play a significant role in the deuterium - neopentane-Pt system.

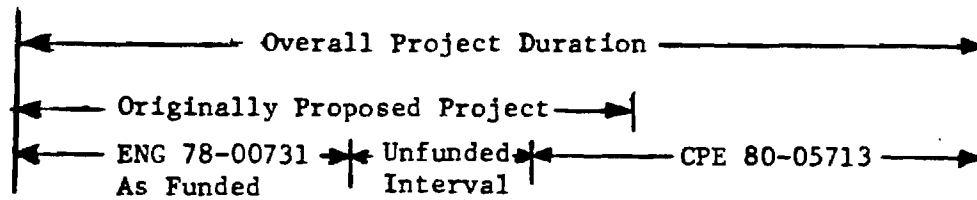
7. Deuterium-neopentane reaction studies over crushed catalyst particles in a batch recirculation reactor have been conducted. These experiments are aimed at determining influence of average Pt crystallite size on reaction rate and desorption parameter. Six catalyst samples, each with a different Pt dispersion, have been run. The reaction has been found to be "facile" over a range of Pt crystallite sizes of 10 to 140 \AA .
8. All computer programs for finding the best parameter values for the two models mentioned in 6 above for any Pt distribution within a catalyst particle have been written and tested.

Table 1 Details of Major Objectives of Project

I. Exploration and development of reproducible techniques for preparing nonuniformly active catalysts	II. Exploration and development of techniques for characterizing catalysts with radially varying activity and diffusivity	III. Reaction experiments	IV. Data analysis and model evaluation
<p>A. Equipment procurement</p> <p>B. Equipment erection</p> <p>C. Acquisition of catalyst supports and other supplies</p> <p>D. Measurement of adsorption isotherm for H_2PtCl_6 and support material</p> <p>E. Investigation of preparation variables</p>	<p>A. Equipment procurement</p> <p>B. Equipment erection</p> <p>C. Total metal content by x-ray fluorescence or spectroscopic method</p> <p>D. Total metal surface area by H_2 chemisorption and x-ray line broadening</p> <p>E. Radial variation of metal crystallite size by T.E.M. of thin sections</p> <p>F. Radial variation of effective diffusivity by unsteady state technique</p>	<p>A. Equipment procurement</p> <p>B. Equipment erection</p> <p>C. Uniform catalyst --effect of ϕ on effectiveness and selectivity</p> <p>D. Catalysts with radially increasing metal profiles (center to surface) --effect of ϕ and metal profile on effectiveness and selectivity</p> <p>E. Catalysts with radially decreasing metal profiles (center to surface) --effect of ϕ and metal profile on effectiveness and selectivity</p> <p>F. Structure sensitivity of D-hydride exchange</p>	<p>A. Computer program for correction of mass spectra for fragmentation and natural abundances</p> <p>B. Preparation of computer programs for models No. 1, 2, and 4 (Ref 3)</p> <p>C. Preparation of computer programs for models No. 3, 5, 6, and 7 (Ref 3)</p> <p>D. Model testing -- comparison of predictions of models No. 1, 2, and 4 with experimental kinetic data (Ref 3)</p> <p>E. Model testing -- comparison of predictions of models No. 3, 5, 6, and 7 with experimental kinetic data (Ref 3)</p>

5.

TABLE 2 Project Time Schedule (Revised) -- Percent to Completion for Major Project Objectives Listed In Table 1.



8/15/78 8/15/79 8/15/80 10/15/80 10/15/81 10/15/82

Objective I

A	100%	0%	0%	0%	0%	0%
B	100	0	0	0	0	0
C	100	0	0	0	0	0
D	100	0	0	0	0	0
E	100	80	0	0	0	0

Objective II

A	100	0	0	0	0	0
B	100	20	0	0	0	0
C	100	0	0	0	0	0
D	100	0	0	0	0	0
E(1)	100	80	80	70	30	0
F(2)	NA	NA	80	70	30	0

Objective III

A	100	0	0	0	0	0
B	100	0	0	0	0	0
C(1)	100	50	30	30	10	0
D(1)	100	100	30	30	10	0
E(1)	100	100	30	30	10	0
F(2)	NA	NA	50	40	10	0

Objective IV

A	100	50	0	0	0	0
B	100	100	0	0	0	0
C(2)	NA	NA	0	0	0	0
D	100	100	30	0	0	0
E(2)	NA	NA	100	100	50	0

- (1) Objective of originally proposed project which were estimated to be completed in third year of project.
- (2) New Objectives which did not appear in original proposal but were conceived while performing work on ENG 78-00731. These objectives were stated in proposal which was funded as CPE 80-05713.

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Yr 2 REPORT

PROGRESS REPORT FOR ENG 78-00731 FOR

THE PERIOD 8/15/79 to 8/15/80

I. INTRODUCTION

During the second year of the program we focused our efforts on

- (1) Utilizing a new technique developed during the first year of the program to prepare seven nonuniformly active catalysts with different types of Pt profiles
- (2) Utilizing a spectrometric technique, X-Ray fluorescence, H_2 chemisorption and EPM in order to characterize these seven catalysts
- (3) Conducting a total of forty-three deuterium-neopentane exchange experiments on the seven catalyst particles over a temperature range of 150 to 280°C.
- (4) Completing all model development, including writing computer programs, for testing kinetic data from item 3 above,
- (5) Conducting deuterium-neopentane exchange reaction studies over crushed catalyst particles in a batch recirculation reactor in order to determine whether average Pt crystallite size has an influence on reaction rate, and
- (6) Testing of a diffusion cell, similar to that of Goring and deRossett (1964), for measuring diffusion coefficients for gases in single catalyst particles.

II. EXPERIMENTAL

A. Equipment

1. Vacuum system (see Reference 2.)
2. Reactor for deuterium-neopentane exchange experiments on single particles (see Reference 2.)
3. Hydrogen chemisorption system (see Reference 2.)
4. Catalyst preparation (see Reference 3.)
5. Diffusion cell (see Reference 2.)
6. Batch recirculation reactor

Fig. 1 shows a batch recirculation reactor which was connected to the vacuum system described in Ref. 2. The reaction system was designed for high space velocity and low conversion per pass. Gas recirculation was achieved by means of an inert, non-contaminating, double acting magnetic pump. Gas recirculation rate was typically 1.5 liters/minute. The reactor was a quartz U-tube packed with crushed catalyst particles.

A Leeds-Northrup zero-voltage power pack supplied power to the furnace surrounding the reactor. Temperature was controlled by a Leeds-Northrup Electromax III proportional controller. A thermowell was positioned at the center of the catalyst bed.

The reaction system was directly connected to the Kratos MS10S mass spectrometer.

B. Procedure

1. Catalyst preparation. (See Reference 3).
2. Single particle reaction experiments. (See Reference 2).
3. Reaction experiments on crushed catalysts in batch recirculation reactor.

A series of catalysts which vary in average Pt crystallite size were prepared by impregnation of γ -alumina beads (Rhone-Poulenc Inc. GQD-30) with chloroplatinic acid. The impregnated catalysts were washed with water, dried in an oven for 2 hours, reduced in flowing hydrogen for 4 hours at 450°C and crushed to pass through a 200 mesh screen. The Pt crystallite size was determined by hydrogen chemisorption and x-ray line broadening.

The kinetic study consisted of measuring the rate and selectivity for the deuterium-neopentane exchange for each catalyst over a wide range of temperatures. Deuterium to neopentane molar ratio was 450 to 1 for each experiment. Between runs on the same catalyst sample, a catalyst pretreatment

3.

was employed which consisted of evacuating the reactor at 10^{-7} torr and 450°C overnight. Kinetic runs made following this procedure were reproducible within experimental error. Less severe treatment as well as hydrogen treatment before each kinetic run did not lead to reproducible kinetic results.

Mass spectroscopic analyses were made at 15eV. Raw data were corrected for fragmentation and natural abundances of C^{13} and deuterium.

4. Diffusion cell testing

Experiments at ambient temperature were conducted on single catalyst particles by a procedure nearly identical to that of Gorring and deRossett (1). The beads employed (Mobil silica/alumina cracking catalyst, G-945) were previously used in Wicke-Kallenbach experiments (4). Diffusivity values for the Wicke-Kallenbach measurements when corrected for molecular weight agreed within 30 percent of values measured by the Gorring-deRossett method. This latter method is currently being employed as a tool to measure diffusivity of neopentane within all single catalyst particles used in kinetic experiments in this study. Future work will also involve measuring diffusivities at elevated temperatures (to 250°C).

III. RESULTS AND DISCUSSION

A. Preparation of catalysts for single particle reaction experiments.

Seven single spherical catalyst particles were designed and prepared for the single bead neopentane-deuterium exchange experiments. All of these catalysts were prepared with either γ -alumina supports (Catalysts D, E, F, H, I) or 90% silica-10% alumina supports (catalysts G and K). Table 1 lists properties of these catalysts. Two catalysts with monotonically decreasing Pt profiles from particle

Table 1: Properties of supported metal catalysts

<u>catalyst</u>	<u>support</u>	<u>pore size</u>	<u>wt(g)</u>	<u>radius (mm)</u>	<u>Pt (wt%)</u>	<u>Particle size(\AA)</u>	<u>Metal surface area (m^2)</u>
D	γ -alumina	450	0.0142	1.90	0.50	10	0.0160
E	γ -alumina	450	0.0134	1.85	0.45	15	0.0098
F	γ -alumina	450	0.0141	1.90	0.51	8	0.0204
H	γ -alumina	450	0.0132	1.85	1.16	7	0.0507
I	γ -alumina	450	0.0134	1.90	0.50	10	0.0151
G	Si/Al	35	0.0342	1.85	0.61	19	0.0238
K	Si/Al	35	0.0217	1.65	0.41	14	0.0167

center to surface (catalysts D and E) were prepared by adding beads to Pt-CA solution for 24 hours. (Pt and CA refer to H_2PtCl_6 and citric acid respectively). Two catalysts with increasing Pt profiles were prepared by adding beads to a Pt solution for 22 hours (catalyst F and I). Two catalysts, H and G, with uniform Pt distributions were prepared in order to provide a comparison of reaction results between uniform and nonuniform catalysts. Catalyst K, with increasing Pt profile on Si/Al, was prepared by adding beads into a concentrated Pt solution for 5 minutes and transferring them immediately to a chamber where they were reduced. This catalyst had a Pt distribution similar to that of catalyst F. Both catalysts G and K have much smaller average pore diameters than D, E, F, I, and H.

B. Catalyst characterization

Pt concentration in the catalyst (Table 1) was determined by spectrophotometric analysis of impregnating solution before and after the impregnation process. Good agreement was found between those results and those of x-ray fluorescence analyses. Average Pt crystallite size was calculated based upon H_2 chemisorption measurements. Typical EPM results can be found in a previous report (3).

Attempts were made to measure the metal particle size variation along the radius of a catalyst particle by transmission electron microscopy (TEM). The specimens were prepared by grinding small amounts of catalyst at different radial positions along the catalyst and placing

6.

the grindings on carbon coated grids. Each grid was then coated with another layer of carbon. The alumina support was dissolved and washed with a 10% HF acid solution. This specimen was examined by TEM. Due to very small metal particle size no particles were observed by TEM. This technique will be employed again on catalysts which contain larger Pt crystallites.

C. Single particle reaction experiments

Forty-three single particle deuterium-neopentane exchange experiments on the seven catalyst particles were conducted over the temperature range, 150 to 280°C. Table 2 lists reaction conditions, including total pressure, temperature and mole fraction of neopentane. Table 3 shows typical analyses of samples from several experiments in terms of deuterated tertiary butyl ions, $C_4D_iH_{9-i}$. These ions produce the most abundant peaks in the mass spectrum of deuterated neopentane; it is convenient to analyse the kinetics in terms t-butyl ions rather than in terms of the less abundant parent ions $C_5D_iH_{12-i}$. The validity of using a truncated system to study the kinetics of deuterium-neopentane exchange has been demonstrated (5).

Table 3 lists, for several experiments, both the concentrations of species a_0 through a_9 , in terms of mole fraction of the deuterides as well as the characteristic species b_0 through b_9 , which were obtained by Wei-Prater analysis using the transformation $\vec{b} = \underline{X} \vec{a}$ (See ref 4). (The values of a_1 have been corrected for fragmentation and natural abundances of carbon 13 and deuterium. Wei-Prater analysis transforms the coupled set of rate equations in the real species, $a(i)$, into a

Table 2 Kinetic Reaction Conditions

Catalyst	Total pressure at reaction temp. (torr)	Temperature(°C)	Mol fraction X(neop)*10 ³
D170	156.7	159.5	0.8462
D190	160.1	180.0	0.8462
D220	162.8	218.3	0.8462
D250	163.4	240.0	0.8462
D280	167.2	268.1	0.8462
E170	143.2	174.4	0.8462
E190	162.2	194.2	0.8462
E210	161.5	211.2	0.8462
E230	165.6	233.3	0.8462
E250	165.4	250.5	0.8462
F150	157.0	152.5	0.8306
F170	161.0	173.0	0.8306
F190	161.1	193.9	0.8306
F210	162.3	211.1	0.8306
F230	165.4	230.0	0.8306
F250	162.7	251.4	0.8306
H150	155.4	145.6	0.8462
H170	157.1	166.5	0.8462
H185	158.7	180.6	0.8462
H200	159.8	195.4	0.8462
H22	336.2	210.0	0.8462
H23	219.2	220.5	0.8462

Table 2 (Continued)

Catalyst	Total pressure at reaction temp. (torr)	Temperature(°C)	Mol fraction X(neop)*10 ³
H150H	122.7	151.1	0.8267
H170H	122.2	171.6	0.8267
H190H	123.9	191.0	0.8267
H210H	129.1	209.4	0.8267
H230H	154.9	230.3	0.8267
I165	160.2	164.5	0.8247
I179	162.0	179.2	0.8247
I193	162.2	193.0	0.8247
I203	162.7	203.6	0.8247
I220	163.5	220.0	0.8247
I230	161.5	230.0	0.8247
G130	119.9	130.8	0.8267
G140	121.2	139.5	0.8267
G150	119.9	147.8	0.8267
G160	131.1	160.0	0.8267
G170	122.6	169.9	0.8267
K160	162.0	164.4	0.8236
K170	159.5	173.6	0.8236
K180	92.0	182.2	0.8236
K190	159.5	193.0	0.8236
K200	154.6	201.1	0.8236

TABLE 3

The image displays a 6x6 grid of 36 small, high-contrast, black and white images. Each image shows a dense, repeating pattern of small, dark, rectangular shapes, resembling a textured surface or a microscopic view. The patterns vary slightly across the grid, but all maintain a high degree of regularity and contrast. The overall effect is a complex, textured mosaic.

Note:

A(1) = Mole Fraction C_4H_9-1

B(1) - Concentration of Characteristic Species.

set of uncoupled differential equations in the characteristic species $b(i)$. Plots of $\ln b(i)$ vs time, or $\ln b(i)$ vs $\ln b(i)$ should produce straight lines. Figures 2 and 3 are typical plots of data from one of the deuterium-neopentane experiments. All of our experiments exhibited this linear behavior.

Experimental values of product concentration were compared with values predicted by a one parameter model which describes a single step deuterium-neopentane exchange in the presence of intraparticle diffusion limitation, and by a two parameter model which describes the exchange reaction in the presence of diffusion and desorption limitations. The one parameter model contains one adjustable parameter ϕ_1 , the Thiele modulus. The two parameter model contains two adjustable parameters, β the desorption parameter, and ϕ_1 . The one parameter model is discussed in detail in ref 6. The two parameter model is a modification of a model employed previously for uniformly active catalysts (4) (7). The Pt profile as determined by EPM is an input function in both of these models.

The best values of ϕ_1 and β which minimized the difference between experimental and predicted product concentrations were obtained by a procedure described in ref 4. In this procedure, the parameters, ϕ_1 and β were adjusted until an objective function ψ was minimized, where:

$$\psi = \frac{\sum_{j=1}^N \sum_{i=1}^9 (a_{i,\text{exp}} - a_{i,\text{calc}})^2}{9 \times N}$$

N = Number of samples taken from the reactor during an experiment. Both $a_{i,\text{exp}}$ and $a_{i,\text{calc}}$ were determined at the same neopentane conversion.

Table 4 lists the optimum parameter values as well as values of the objective function, ψ , for both models. By comparing values of the objective function it can be concluded that the one parameter model produces a fit of the kinetic data comparable to that of the two parameter model only at the lower temperatures where desorption influences are small. Thus, contrary to our earlier expectations (8), β effects are important in the deuterium-neopentane-Pt system and must be accounted for in modelling studies.

Figures 4, 5 and 6 are plots of mole fractions of deuterated t-butyl ions versus fractional conversion of neopentane showing typical agreement between experimental data (points) and predictions (solid lines). The solid lines were calculated by model equations using best parameter values obtained for the experimental data. Comparison of Figures 4 and 6 shows the improved data fit by the two parameter model.

D. Influence of Pt crystallite Size on Reaction Rate and Desorption Parameter.

Table 5 lists the average crystallite sizes for six crushed catalyst samples employed in this series of runs.

Kinetic data were analyzed by the Wei-Prater method. Experimental values of product concentration were compared with values predicted by a one parameter model which described the influence of desorption (or β effects) on reaction rate and selectivity.

Table 6 contains kinetic parameter k , desorption parameter β , selectivity M and objective function ψ . The low value of ψ shows that good agreement between experimental data and model predictions occurred for each experiment.

TABLE 4. Comparison of One and Two Parameter Models

Experiment	One Parameter Model		Two Parameter Model	
	ϕ	$\psi \times 10^3$	ϕ	$\psi \times 10^3$
D170	0.1581	2.93	0.1518	0.0060
D190	0.3156	3.45	0.3000	0.0185
D220	0.9894	6.78	0.9517	0.0572
D250	1.4203	20.08	1.0047	0.7383
D280	2.6844	28.15	1.6562	1.1269
E170	0.4117	8.861	0.3648	0.0565
E190	0.9443	4.79	0.9100	0.0399
E210	1.8892	14.42	1.6455	0.3998
E230	3.6742	17.41	2.7898	0.4653
E250	7.7660	30.92	10.2222	0.6620
E150	0.4920	5.01	0.4790	0.0102
E170	1.0397	6.88	0.9960	0.0384
E185	1.5314	10.48	1.3314	0.2085
E200	1.8991	15.49	1.3680	0.5451
E22	3.3356	23.70	2.4949	0.8247
E23	5.0047	38.77	3.6328	1.4371
E150H	-	-	0.3750	0.2250
E170H	-	-	1.1278	0.3460
E190H	-	-	1.6481	0.2138
E210H	-	-	6.5650	1.2220
E230H	-	-	13.1260	1.5030
I165	0.6585	5.02	0.6554	0.0050
I179	1.1288	7.49	0.7663	0.2755
I193	1.8435	9.35	1.4466	0.3329
I203	2.8414	14.87	2.3039	0.4757
I220	4.0374	19.68	4.4155	0.5536
I230	4.5181	29.28	5.3243	0.7954
P150	-	-	0.1921	0.1815
P170	-	-	1.5839	0.1566
P190	-	-	3.0642	0.2865
P210	-	-	5.0321	0.5496
P230	-	-	9.9550	0.7804
C130	-	-	3.0491	0.0000
C140	-	-	3.5636	0.0050
C150	-	-	4.5582	0.0050
G160	-	-	4.1035	0.2398
G170	-	-	7.6732	0.3560
K160	-	-	2.5411	0.0832
K170	-	-	3.2472	0.1551
K180	-	-	11.8720	0.4731
K190	-	-	15.4841	1.0535
K200	-	-	11.9252	0.8473

TABLE 5
CATALYST PROPERTIES

Catalyst	Pt%	D(A°)	
		H ₂ - Chemisorption	X-Ray
Pt10	0.28	< 10	-
Pt19	1.95	19	-
Pt48	2.03	48	50
Pt64	2.23	64	61
Pt70	2.26	70	75
Pt139	2.08	139	143

TABLE 6

EXPERIMENT PARAMETERS

	$T^{\circ} K$	$k_p \cdot 10^3 / \text{sec-gPt}_s$	β	M	$\psi \times 10^3$
PT10	380	1.523	.080	1.07	3.1
	357	.517	.021	1.02	1.4
	338	.183	0.0	1.0	1.6
	319	.086	0.0	1.0	0.6
	400	3.253	.321	1.27	3.6
PT19	402	3.866	1.090	1.86	2.4
	383	1.498	0.438	1.37	2.0
	359	.0403	0.150	1.13	1.4
	343	0.137	0.053	1.05	1.2
	420	7.324	2.020	2.46	2.9
	324	0.053	0.024	1.02	1.6
	402	1.426	0.352	1.30	3.0
PT48	383	0.758	0.106	1.09	2.0
	416	2.434	0.661	1.55	5.3
	365	0.259	0.021	1.07	3.1
	353	0.222	0.011	1.01	1.7
	368	0.547	0.238	1.21	1.1
PT64	377	1.092	0.246	1.21	4.3
	351	0.284	0.094	1.08	5.8
	338	0.177	0.034	1.03	2.3
	324	0.079	0.025	1.02	3.3
	404	3.557	0.702	1.58	3.9
	390	1.561	0.455	1.38	3.2
PT70	378	1.434	0.194	1.17	1.5
	319	0.033	0.009	1.01	1.3
	362	0.476	0.071	1.06	1.4
	404	3.463	0.639	1.53	9.4
	404	3.035	0.614	1.51	4.3
	342	0.131	0.031	1.03	0.7
	342	0.103	0.029	1.03	1.2
	377	1.081	0.146	1.13	3.3
	377	0.956	0.137	1.12	2.2
	407	2.036	1.040	1.83	2.5
	419	3.572	1.311	2.02	1.6
PT139	392	1.263	0.550	1.46	3.1
	374	0.741	0.421	1.36	4.3
	361	0.453	0.300	1.26	4.6

For each catalyst, activation energy was determined by an Arrhenius plot. An example of such a plot is shown in Fig. 7. Table 7 contains activation energy as well as specific activity at 403K for each catalyst.

Reasonably constant values of activation energy, 55 ± 6 kJ/mol, and specific activity, $2.1 \times 10^{-5} \pm 0.5 \times 10^{-5}$ gmol neopentane/sec. gm surface Pt at 403°K, were obtained. It can be concluded that the deuterium-neopentane exchange reaction over supported Pt on γ - alumina is not structure sensitive and can be classified as "facile" according to Boudart's terminology.

TABLE 7

ACTIVATION ENERGY AND SPECIFIC ACTIVITY

	E (kJ/mole)	k^1 (gmoles neopentane/sec - gPts) @ 403 K
PT10	48.94	2.33×10^{-5}
PT9	59.88	2.45×10^{-5}
PT20	49.69	1.60×10^{-5}
PT24	49.92	1.85×10^{-5}
PT34	60.88	2.31×10^{-5}
PT99	55.01	1.80×10^{-5}

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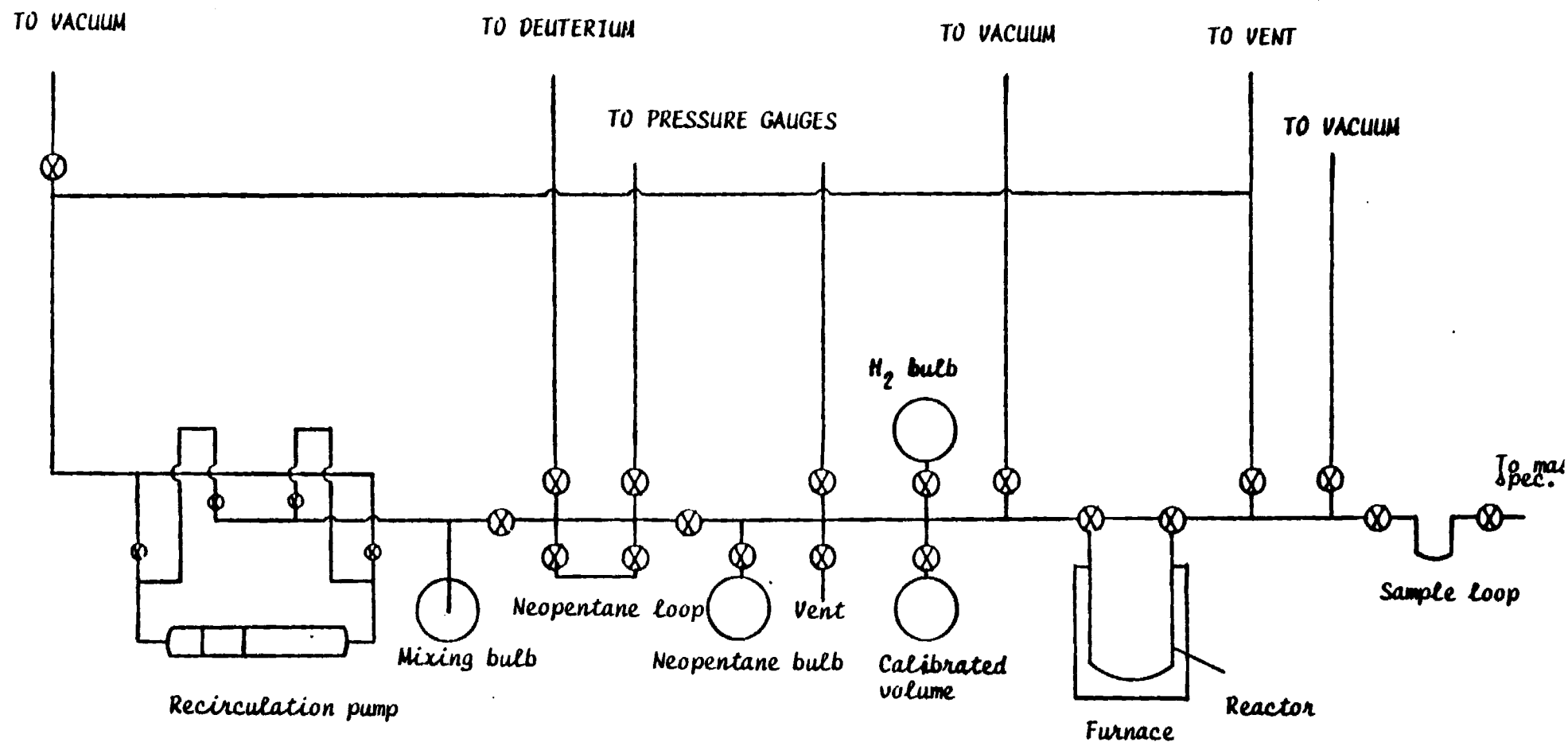


Fig 1. Gas Recirculation Reactor

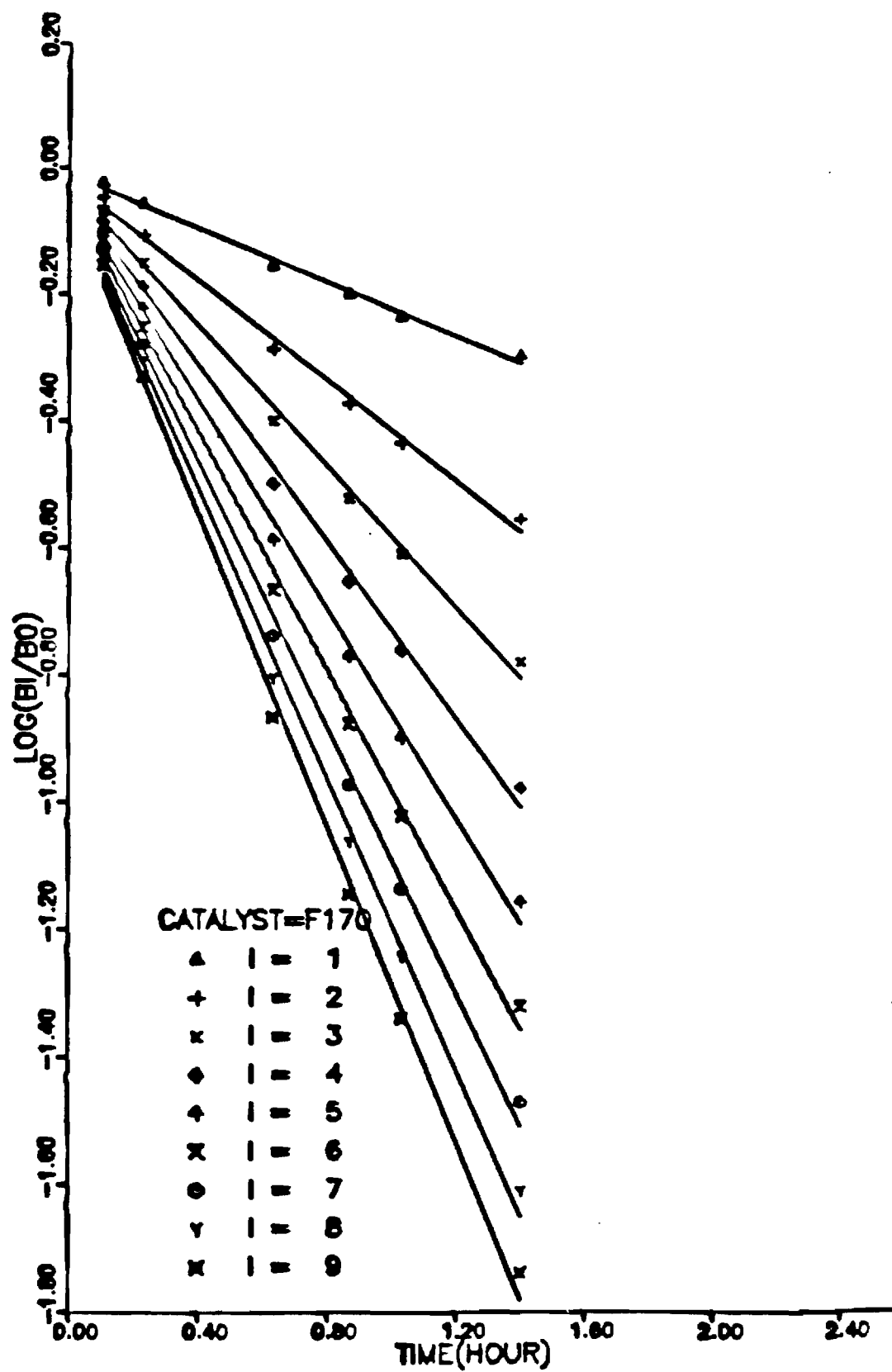


Fig. 2: Decrease of Characteristic Species of Catalyst F170

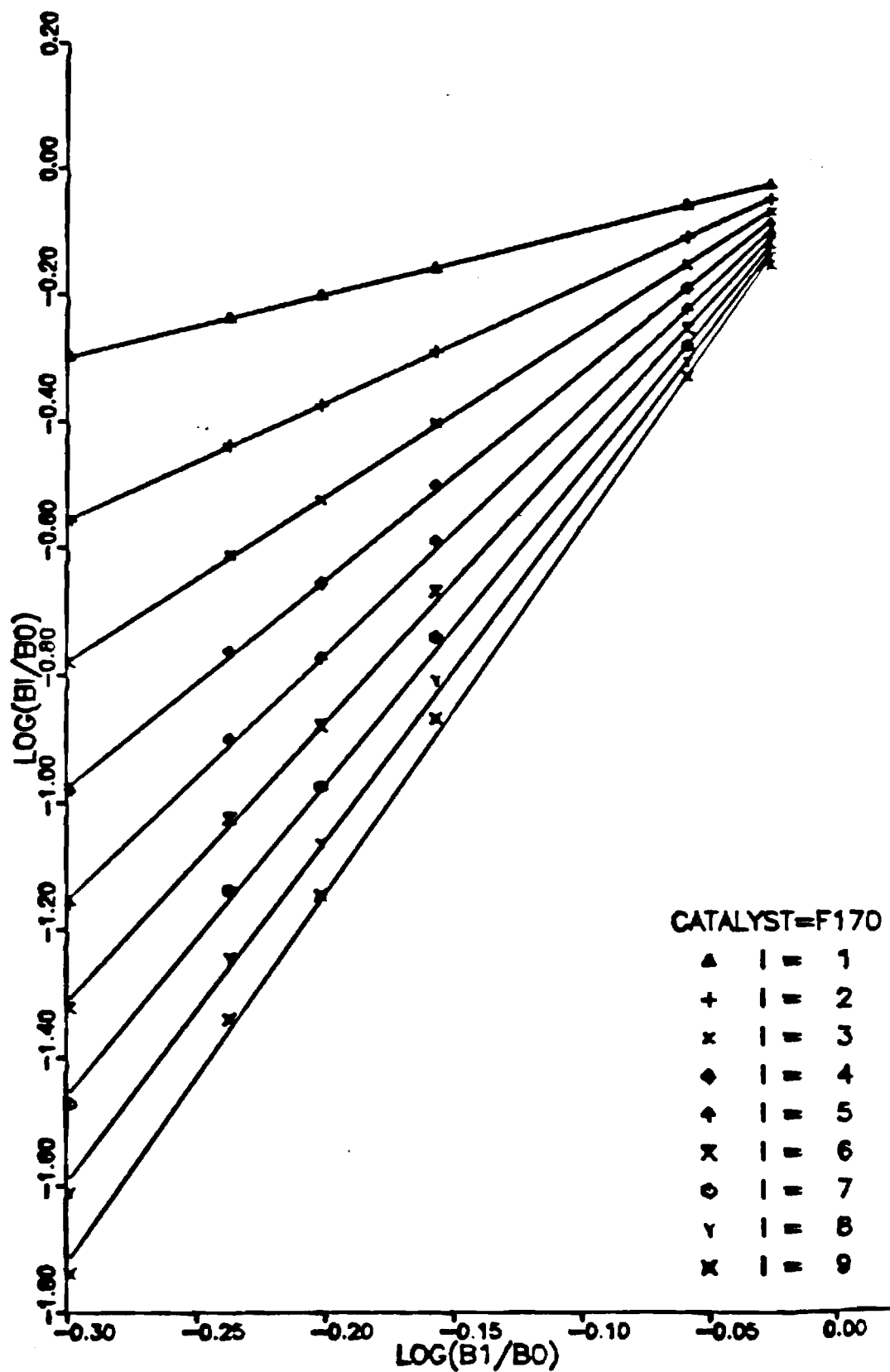


Fig. 3: Logarithmic Relationship between Characteristic Species of Catalyst F170

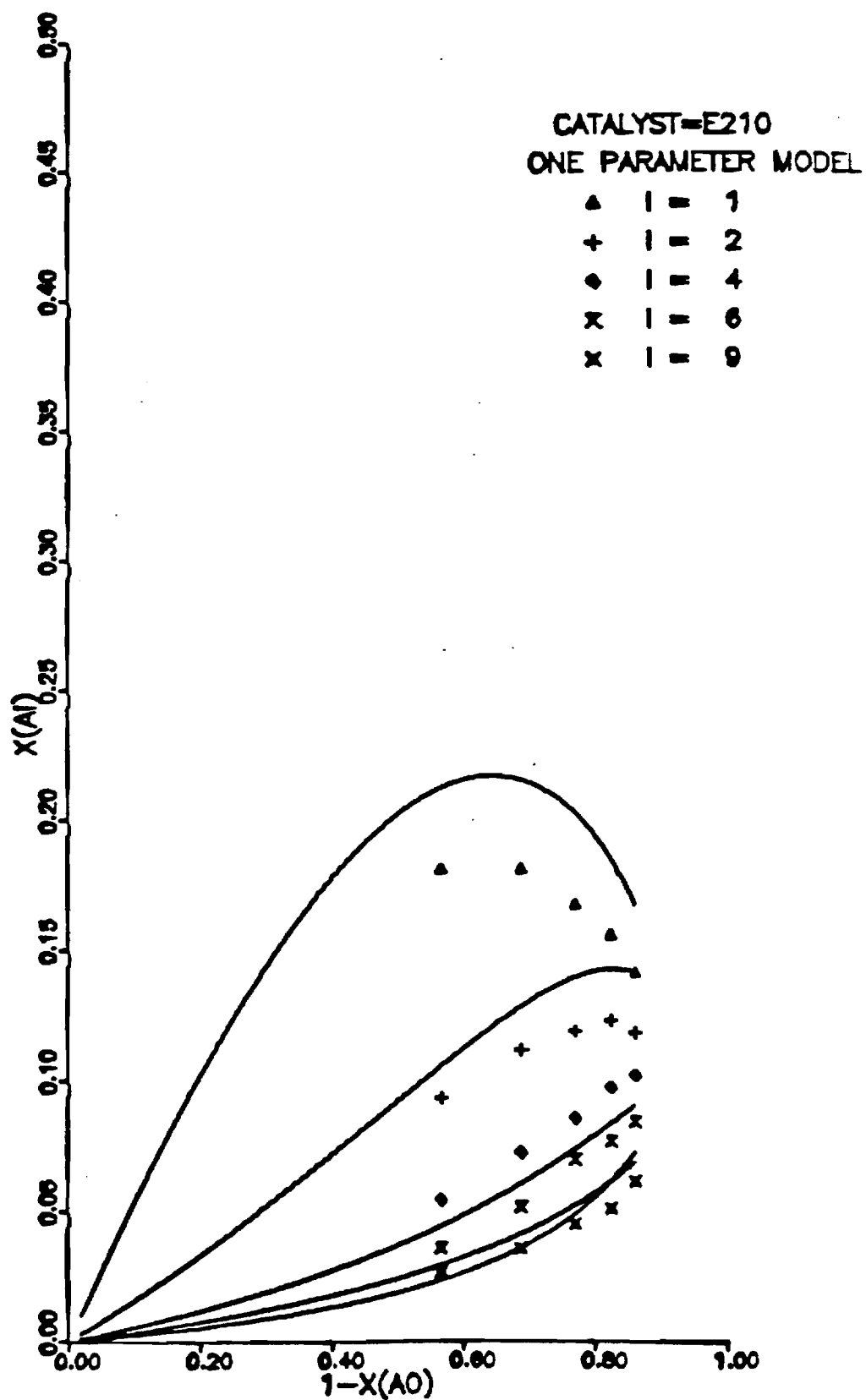


Fig. 4 : Product Distribution of Deuterides by One Parameter Model for Catalyst E210

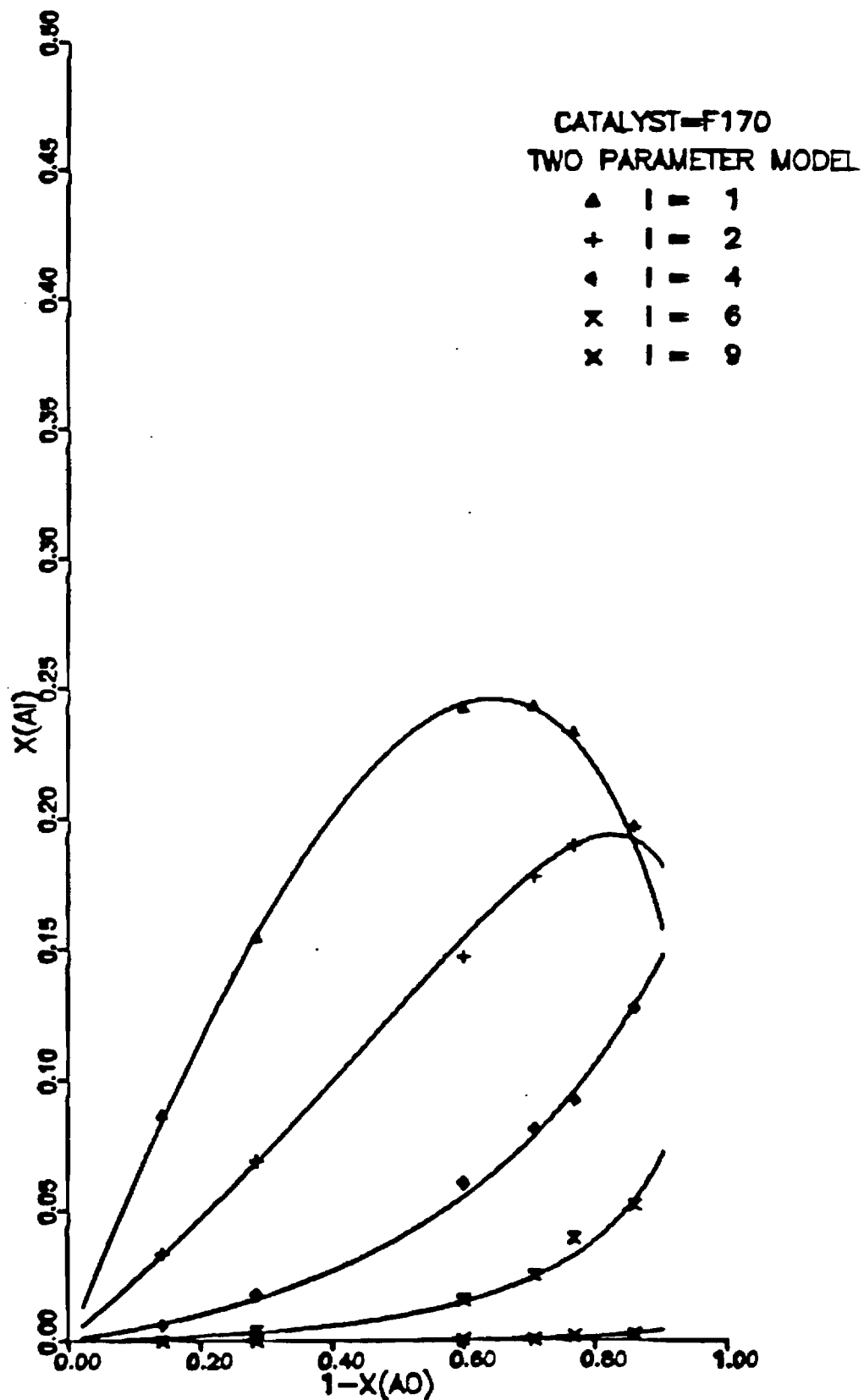


Fig. 5 : Product Distribution of Deuterides by Using New Deuterides
Mole Fraction Objective Function for Catalyst F170

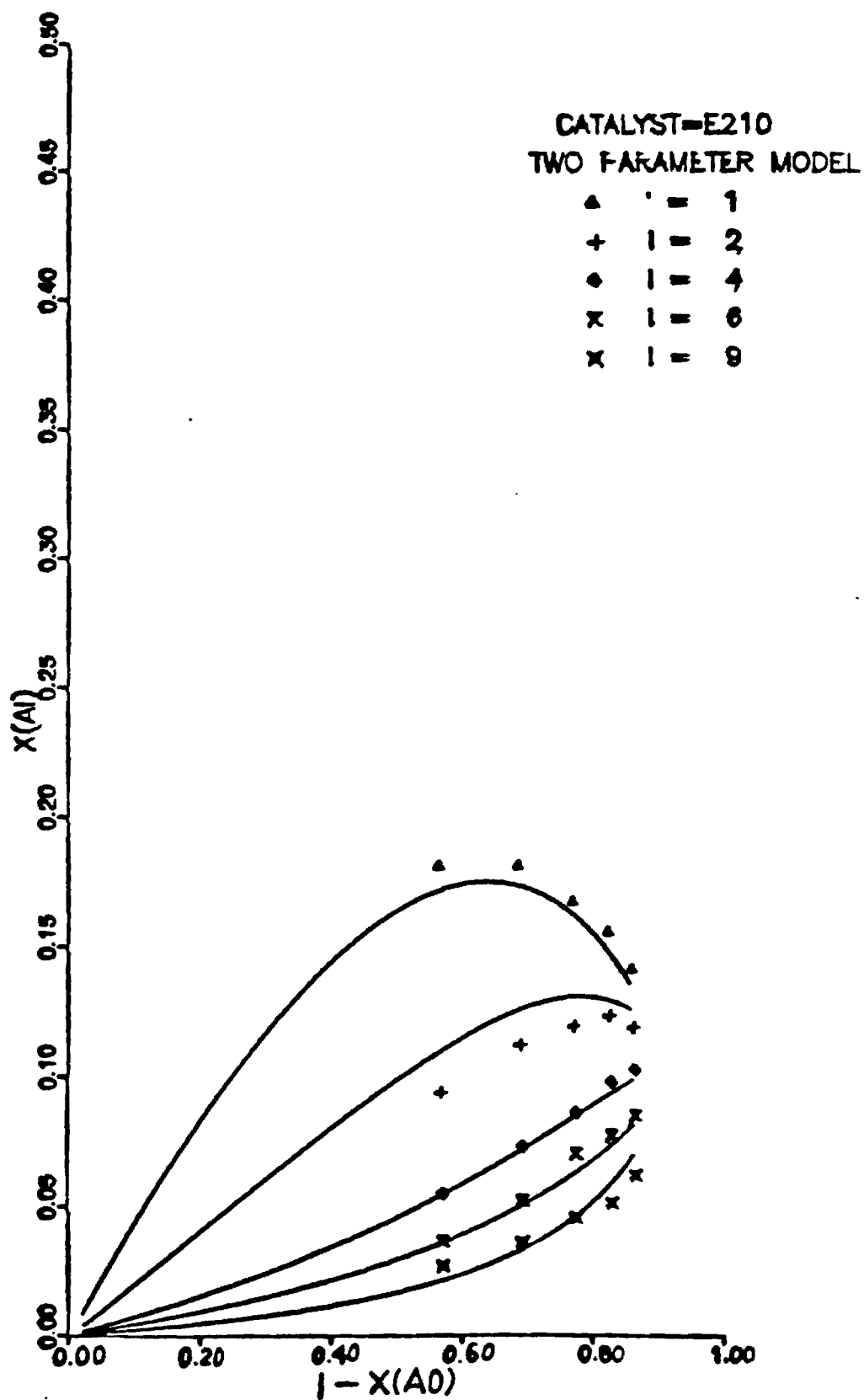


Fig. 6: Product Distribution of Deuterides by Using New Deuterides Mole Fraction Objective Function for Catalyst E210

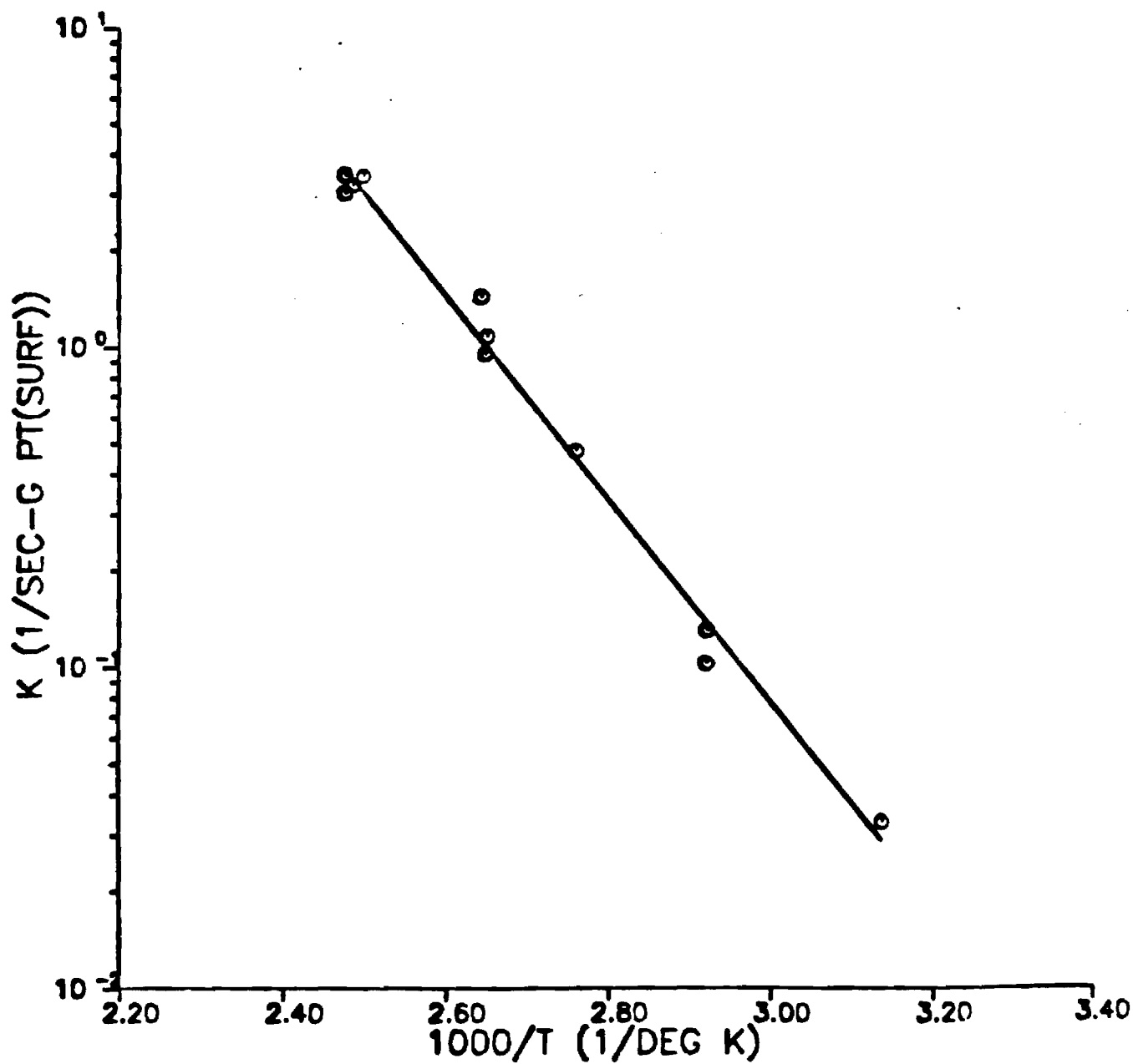


Fig 7: Arrhenius Plot For Pt70